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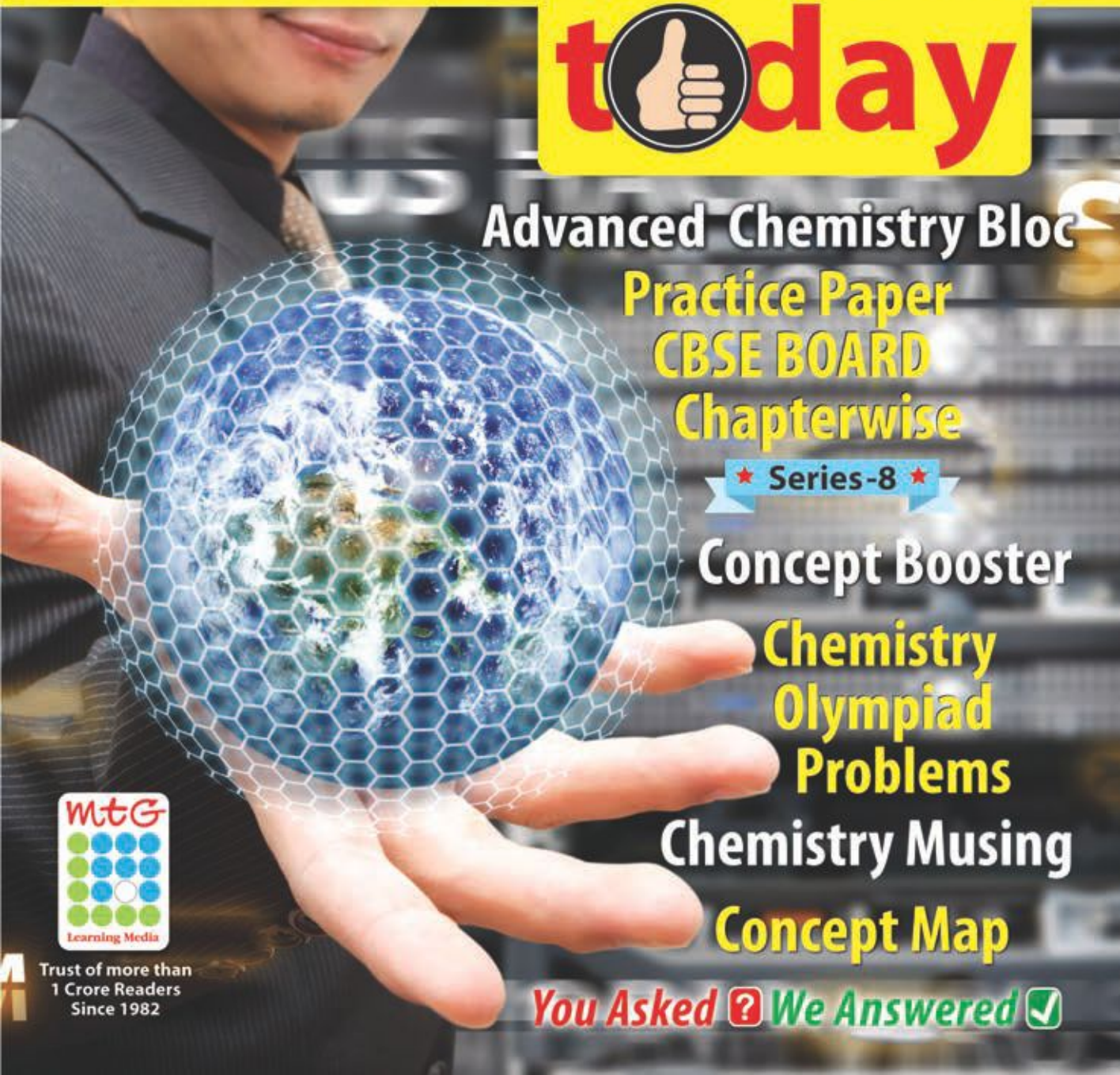
Examiner's Mind
CLASS XI | CLASS XII

CHEMISTRY today



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Chemistry Musing

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Contents

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Editor : Anil Ahlawat

editorial

Chemistry, Analytical Chemistry and Synthesis of Materials

Analysis and synthesis are the two sides of the same coin.

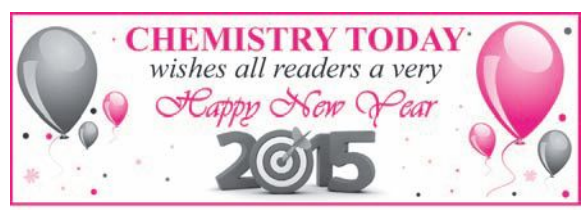
In material science, one is interested in the production of very pure metals, alloys and polymers as well as many other things.

For any material to be useful in reactors – whether it is feed, cladding, the most important quality is purity. Even a few parts per million impurity is enough to affect the working of the reactor. One does not discuss the impurities in percentage quantities.

If the study involves petroleum products such as petrol, diesel or lubricants, used in cars, transport vehicles for materials or in aviation, quality control is very important. Many standards are available, each set for one type of analysis in different concentration levels as well as materials. The same concentration of impurities in different materials give different values of concentration. It is also difficult to obtain different standards of different concentrations to analyse every type of material, even slightly differing in concentration.

It is here, the various research and development centres have to play their very important role. It is here, our brilliant students of pure science subjects as well as engineers find their career to become great research scientists. One need not go overseas to find a good career. The difference in salary between developing countries and India will be compensated by the freedom to work in the big laboratories in India which are well-known all over the world.

Anil Ahlawat
Editor



CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

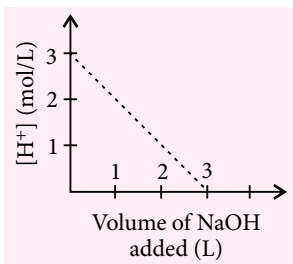
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 18

JEE MAIN/PMTs

1. 1 M NaOH solution was slowly added to 1 L of 210 g impure H_2SO_4 solution and the following plot was obtained.



The percentage purity of H_2SO_4 sample is

(a) 70 % (b) 80 %

(c) 75 % (d) none of these.

2. Bromine, Br_2 boils at 58.8 °C, while iodine monochloride, ICl boils at 97.4 °C. The main reason ICl boils almost 40 °C higher than Br_2 is that

(a) the molecular weight of ICl is 162.4 while that of Br_2 is 159.8

(b) ICl is covalent compound, while Br_2 is ionic

(c) London dispersion forces are stronger for ICl than that for Br_2

(d) ICl is polar, while Br_2 is non-polar.

3. Although aldehydes and ketones also contain a carbonyl group, like acid halides they do not undergo nucleophilic substitution reactions because

(a) they do not have electronegative chlorine atom

(b) carbon atom of carbonyl group in aldehydes and ketones is less electron deficient

(c) hydride ion and methylide ion are strong bases and hence are poor leaving groups

(d) none of the above.

4. All the oxygen in a 0.5434 g sample of a pure oxide of iron is removed by reduction in a stream of H_2. The loss in weight is 0.1210 g. Hence, formula of the iron oxide is (Fe = 56)

(a) FeO (b) Fe_2O_3

(c) Fe_3O_4 (d) FeO_2

Solution Senders of Chemistry Musing

SET 17

1. Pijush Kanti Roy (West Bengal)
2. Agranipanda
3. Kashish Arora (Haryana)
4. Ronal Gaonkhowa (Assam)

SET 16

1. Sayantan Adhikary (West Bengal)
2. Rajesh Kumar Yadav (Kanpur)

5. An aliphatic organic compound containing C, H and N reacts with dilute HCl to produce formic acid. It is reduced to dimethylamine by Pt or Ni, and undergoes addition reactions with chlorine and sulphur. The compound can be
(a) CH_3NC
(b) CH_3CN
(c) CH_3NH_2
(d) a mixture of (a) and (b).

JEE ADVANCED

6. Compound (*A*) $C_5H_8O_2$ liberated CO_2 on reaction with sodium bicarbonate. It exhibits geometrical isomerism. It gave compound (*B*), $C_5H_{10}O_2$ on hydrogenation. Compound (*B*) can be separated into enantiomorphs. Structures of (*A*) and (*B*) respectively are
(a) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-COOH$,
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-COOH$
(b) $CH_3-CH=\underset{\underset{CH_3}{|}}{C}-COOH$,
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-COOH$
(c) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH$,
$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-COOH$
(d) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-COOH$,
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH$

COMPREHENSION

A protein with a specific biological activity has a unique three-dimensional structure called its native shape. When a protein in its native form is subjected to change of temperature or pH or is exposed to heavy metal salts such as Hg^{2+}, Pb^{2+}, etc., the native shape of the protein is destroyed and biological activity is lost. Such a protein is called denatured protein. In most of the cases, the process of denaturation is irreversible but in some cases it may also be reversible.

7. Denaturation of proteins leads to loss of its biological activity by
(a) formation of amino acids
(b) loss of primary structure
(c) loss of both primary and secondary structures
(d) loss of both secondary and tertiary structures.

8. Which of the following statements is incorrect about denaturation of proteins?
(a) The primary structure of the protein does not change.
(b) Globular proteins are converted into fibrous proteins.
(c) Fibrous proteins are converted into globular proteins.
(d) The biological activity of the protein is destroyed.

INTEGER VALUE

9. Total number of isomers possible for the complex ion $[Cr(NH_3)(OH)_2Cl_3]^{2-}$ is

10. The rate constant of a reaction increases by 8% when its temperature is raised from 400 K to 410 K, while its equilibrium constant increases by 3%. The sum of the activation energies of the forward and reverse reactions is $x \times 10^3$ cal, x is

EXAMINER'S MIND CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. When 80 mL of 0.20 M HCl is mixed with 120 mL of 0.15 M KOH, the resulting solution is the same as a solution of
(a) 0.16 M KCl and 0.02 M HCl
(b) 0.08 M KCl
(c) 0.08 M KCl and 0.01 M KOH
(d) 0.08 M KCl and 0.01 M HCl.

2. In the dehydration reaction,

$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3C{\equiv}N$

the hybridisation state of carbon changes from
(a) sp^3 to sp^2 (b) sp to sp
(c) sp^2 to sp (d) sp to sp^3.

3. The AsF_5 molecule is trigonal pyramidal. The hybrid orbitals used by the As atoms for bonding are
(a) $d_{x^2-y^2}$, d_{z^2}, s, p_x, p_y (b) d_{xy}, s, p_y, p_z
(c) s, p_x, p_y, p_z , d_{z^2} (d) $d_{x^2-y^2}$, s, p_x, p_y, p_z

4. Mg_2C_3 reacts with water forming propyne. C_3^{4-} has
(a) two sigma and two pi bonds
(b) three sigma and one pi bonds
(c) two sigma and one pi bonds
(d) two sigma and three pi bonds.

5. An organic compound has C and H percentage in the ratio 6 : 1 and C and O percentage in the ratio 3 : 4. The compound is
(a) HCHO (b) CH_3OH
(c) CH_3CH_2OH (d) $(COOH)_2$

6. Which of the following mixtures cannot be prepared?
(a) $NaHCO_3 + Na_2CO_3$
(b) $Na_2CO_3 + NaOH$
(c) $NaHCO_3 + NaOH$
(d) $H_2CO_3 + NaHCO_3$

7. If E_1, E_2, and E_3 represent the kinetic energies of an electron and an alpha particle and a proton respectively, each having same de-broglie wavelength then
(a) $E_1 > E_3 > E_2$ (b) $E_2 > E_3 > E_1$
(c) $E_1 > E_2 > E_3$ (d) $E_1 = E_2 = E_3$

8. One mole $N_2O_{4(g)}$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% of $N_2O_{4(g)}$ decomposes to $NO_{2(g)}$. The resultant pressure is
(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm

9. In Kjeldahl's method for the estimation of N_2, potassium sulphate and copper sulphate are used. The function of them is
I. Potassium sulphate raises the b.pt. of H_2SO_4 and thus, ensures complete reaction.
II. Copper sulphate acts as catalyst.
III. Potassium sulphate acts as catalyst and copper sulphate raises the b.pt. of H_2SO_4.

Which of these is correct?
(a) Only III (b) Both I and II
(c) Only II (d) None of these.

10. The signs for ΔH, ΔS and ΔG for the freezing of liquid water at –10°C respectively are
(a) +, –, + (b) –, –, 0
(c) –, +, – (d) –, –, –

11. To which orbit the electron in the hydrogen atom will jump on absorbing 12.1 eV of energy?
(a) II orbit (b) III orbit
(c) IV orbit (d) V orbit

12. Which pair of elements belongs to same group?
(a) Elements with atomic no. 17 and 38.
(b) Elements with atomic no. 20 and 40.
(c) Elements with atomic no. 17 and 53.
(d) Elements with atomic no. 11 and 33.

13. The self ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. The density of formic acid is 1.22 g cm^{-3}. The percentage dissociation of formic acid is
(a) 0.002 % (b) 0.004 %
(c) 0.006 % (d) 0.008 %

14. The compound X (C_5H_8) reacts with ammoniacal $AgNO_3$ to give a white precipitate and on oxidation with hot alkaline $KMnO_4$ gives the acids, $(CH_3)_2CHCOOH$. Therefore, X is
(a) $CH_2=CHCH=CHCH_3$
(b) $CH_3(CH_2)_2C\equiv CH$
(c) $(CH_3)_2CH-C\equiv CH$
(d) $(CH_3)_2C=C=CH_2$

15. Le Chatelier's principle is valid for
(a) formation of molasses
(b) rectification of dilute alcohol
(c) manufacture of H_2SO_4 by Contact process
(d) manufacture of acid by vinegar process.

16. $(C_5H_5)^-$ is a/an
(a) non-aromatic compound
(b) anti-aromatic compound
(c) aromatic compound
(d) sometimes behaves as an aromatic and sometimes as a non-aromatic compound.

17. H_3BO_3 is
(a) monobasic and weak Lewis acid
(b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid
(d) tribasic and weak Bronsted acid.

18. $\underset{\text{Colourless salt}}{A} \xrightarrow{\Delta} \underbrace{B+C}_{\text{Gas}} + D;\ D \xrightarrow{H_2O} E.$

Gas 'C' turns solution 'E' milky. 'B' burns with blue flame. 'A' also decolourises MnO_4^-/H^+.
A, B, C, D and E respectively are
(a) CaC_2O_4, CO, CO_2, CaO, $Ca(OH)_2$
(b) CaC_2O_4, CO_2, CO, CaO, $Ca(OH)_2$
(c) $CaCO_3$, CO, CO_2, $Ca(OH)_2$, CaO
(d) $CaOCl_2$, Cl_2, O_2, CaO, $Ca(OH)_2$

19. Which of the following salts is sparingly soluble in water?
(a) $BeSO_4$ (b) $MgSO_4$
(c) $CaSO_4$ (d) $BaSO_4$

20. Which is most stable out of the following?
(a) $[Be(H_2O)_4]^{2+}$ (b) $[Mg(H_2O)_4]^{2+}$
(c) $[Ca(H_2O)_4]^{2+}$ (d) $[Sr(H_2O)_4]^{2+}$

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. The dissociation of ammonium carbamate may be represented by the equation,
$NH_2COONH_{4(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
$\Delta H°$ for the forward reaction is negative. The equilibrium will shift from right to left if there is
(a) a decrease in pressure
(b) an increase in temperature
(c) an increase in the concentration of ammonia
(d) an increase in the concentration of carbon dioxide.

22. Which of the following statements is/are correct?
(a) Alkali metals are better reducing agents than alkaline earth metals.
(b) SF_6 is well known but SH_6 is not known.
(c) BCl_3 is a stronger Lewis acid than BF_3.
(d) Boron forms B^{3+} ions.

23. A gas described by van der Waals equation

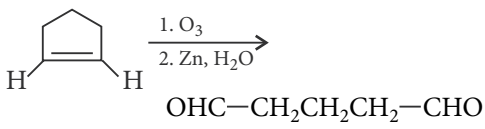
(a) behaves similar to an ideal gas in the limit of large molar volumes

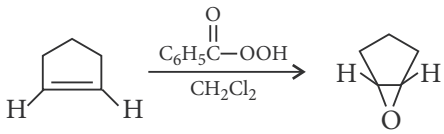
(b) behaves similar to an ideal gas in the limit of large pressures

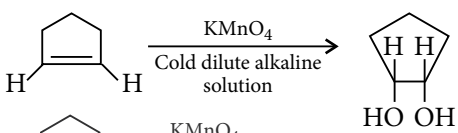
(c) is characterised by van der Waals coefficients that are dependent on identity of the gas

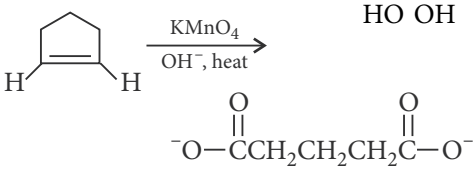
(d) none of the above is correct.

24. Which of the following are correct?

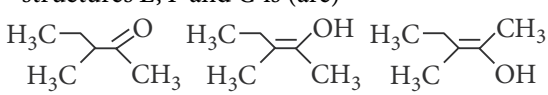
(a) 

(b) 

(c) 

(d) 

25. The correct statement(s) concerning the structures *E*, *F* and *G* is (are)



(a) *E*, *F* and *G* are resonance structures.

(b) *E*, *F* and *E*, *G* are tautomers.

(c) *F* and *G* are geometrical isomers.

(d) *F* and *G* are diastereomers.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Ethane molecule contains a carbon–carbon single bond with each carbon atom attached to three hydrogen atoms. Rotation around C—C single bond results into infinite number of spatial arrangements called conformational isomers.

Repulsive interaction between the electron clouds which affects the stability of a conformation is called torsional strain. Magnitude of torsional strain depends upon the angle of rotation around C—C bond called dihedral angle.

26. Which of the following statements is correct?

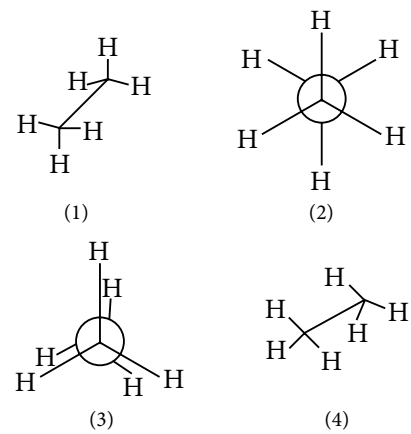
(a) Ethane has two conformations of which staggered conformation is more stable than the eclipsed conformation.

(b) Ethane has an infinite number of conformations of which eclipsed conformation is more stable than the staggered conformation.

(c) Ethane has an infinite number of conformations of which staggered conformation has the maximum energy.

(d) Ethane has an infinite number of conformations of which the staggered conformation is possessed by majority of the molecules at room temperature.

27. In the following structures, which two forms are staggered conformation of ethane?



(a) 1 and 4 (b) 2 and 3

(c) 1 and 2 (d) 1 and 3

28. The dihedral angle between the hydrogen atoms of two methyl groups in staggered conformation of ethane is

(a) 120° (b) 60°

(c) 90° (d) 180°

Paragraph for Questions 29 to 31

In case of mechanical work if the pressure is not constant at every stage of compression, but it changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\Sigma P\Delta V$.

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation,

$$w = -\int_{V_i}^{V_f} P_{ex} dV$$

Such processes are called reversible processes. Processes other than reversible processes are known as irreversible processes.

29. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is (1 L atm = 101.3 J)

(a) – 6 J (b) – 608 J

(c) + 304 J (d) – 304 J

30. One mole of an ideal gas is allowed to expand freely and adiabatically into vacuum until its volume has doubled. The expression which is not true about the given statement is

(a) $\Delta H = 0$ (b) $\Delta S = 0$

(c) $\Delta U = 0$ (d) $W = 0$

31. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in the figure.

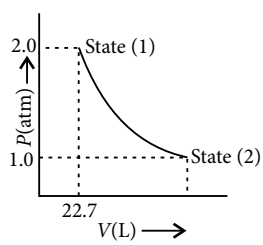
Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

(a) –1786.2 J

(b) 1717.46 J

(c) 1.71746 J

(d) –1717.46 J



SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the change of pressure or temperature given in List I with the description given in List II and select the correct answer using the code given below the lists :

List I		List II
P.	P is increased	1. Solubility of KCl in H_2O is increased.
Q.	P is decreased	2. Solubility of gas in H_2O is increased.
R.	T is increased	3. Dissociation of PCl_5 is increased.
S.	T is decreased	4. Exothermic reaction moves in forward direction.

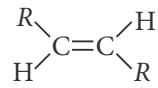
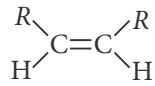
	P	Q	R	S
(a)	4	2	1	3
(b)	2	3	1	4
(c)	3	1	2	4
(d)	2	3	4	1

33. Match the name of the compound given in List I with its formula given in List II and select the correct answer using the code given below the lists :

List I		List II
P.	Borax	1. SiC
Q.	Carborundum	2. $Na_2B_4O_7.10H_2O$
R.	Borazine	3. Na_2SiO_3
S.	Water glass	4. $B_3N_3H_6$

	P	Q	R	S
(a)	2	1	4	3
(b)	3	1	2	4
(c)	1	4	2	3
(d)	4	2	1	3

34. Match the reactants and reagents given in List I with the final products given in List II and select the correct answer using the code given below the lists :

List I		List II
P.	$R-C\equiv C-R \xrightarrow{PtO_2 \text{ or } (C_6H_5)_3P]_3}$	1. 
Q.	$R-C\equiv C-R \xrightarrow{Li\text{-}NH_3,\ C_2H_5OH}$	2. RCH_2CH_2R
R.	$R-C\equiv C-R \xrightarrow{Pd/CaCO_3}$	3. 
S.	$R-C\equiv C-R \xrightarrow[H_2O_2,OH^-]{BH_3,THF}$	4. $RCH_2\overset{\overset{O}{\|}}{C}R$

	P	Q	R	S
(a)	1	3	2	4
(b)	2	1	4	3
(c)	2	1	3	4
(d)	1	2	3	4

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** N_2 and NO^+ both are diamagnetic substances.
Reason : NO^+ is isoelectronic with N_2.

36. **Assertion :** Helium shows only +ve deviations from ideal behaviour.
Reason : Helium is an inert gas.

37. **Assertion :** The O—O bond length in H_2O_2 is shorter than that of O_2F_2.
Reason : H_2O_2 is an ionic compound.

38. **Assertion :** Glycerol can be purified by distillation under reduced pressure.
Reason : Liquid organic compounds are purified by distillation.

39. **Assertion :** Singlet carbene has a linear structure.
Reason : The carbon atom in singlet carbene is *sp*-hybridised.

40. **Assertion :** The lower the concentration of D.O. the more polluted is the water.
Reason : Oxygen is consumed by microbes for the decomposition of organic matter present in water.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

42. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 10 atm pressure. Due to a hole in the vessel the gas leaks out. The ratio of rate of diffusion of He to that of CH_4 is

43. A hydrocarbon $W(C_6H_{10})$ gave a white precipitate with ammoniacal silver nitrate. Oxidation of *W* with hot alkaline $KMnO_4$ gave 2,2-dimethylpropanoic acid. The number of sp^2 hybridised C-atoms in *W* is

44. The silver salt of an alkyne contains 67.08 % of silver. If no other functional group is present, then number of carbon atoms in alkyne is

45. Among the following, the number of underlined elements having +6 oxidation state is
$\underline{P}O_4^{3-}$, $H_2\underline{S}_2O_8$, $H_2\underline{S}O_5$, $\underline{O}F_2$, $\underline{Cr}_2O_7^{2-}$, $\underline{Cr}O_5$

46. Compounds *X* and *Y* are obtained by the reaction of Cl_2 with cold and dil. NaOH and compounds *X* and *Z* are formed with hot and conc. NaOH. The oxidation state of the cation in *Y* is

47. X has exceptional outer electronic configuration as $4d^{10}\ 5s^0$. Period to which it belongs is

48. Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as

frequency $\upsilon = 3.29 \times 10^{15}\,(\text{Hz})\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$.

The value of n if the transition is observed at 1285 nm is

49. When excess NaOH solution is added to Pb^{2+} salt a clear solution (Y) is obtained. When H_2O_2 is added to (Y) a black ppt., (Z) is obtained. The change in oxidation state of Pb is

50. 1 mole of NO_2 and 2 moles of CO are introduced in a 1 litre closed vessel to get the following equilibrium.

$$NO_{2(g)} + CO_{(g)} \rightleftharpoons NO_{(g)} + CO_{2(g)}$$

At equilibrium point 25% of the initial amount of $CO_{(g)}$ was reacted, then K_c for the above reaction is $1/x$. The value of x is

SOLUTIONS

1. **(c) :** 80 mL of 0.20 M HCl = 80 × 0.2
= 16 millimoles

120 mL of 0.15 M KOH = 120 × 0.15
= 18 millimoles

As $\underset{(HCl)}{M_1V_1} < \underset{(KOH)}{M_2V_2}$

Thus, resulting solution is basic containing KCl and unreacted KOH,

$$KOH + HCl \rightarrow KCl + H_2O$$

$$[KOH]_{unreacted} = \frac{M_2V_2 - M_1V_1}{V_1 + V_2} = \frac{18-16}{200}$$
$$= 0.01\ M$$

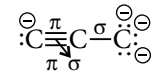
KCl formed = HCl used
= 16 millimoles
= 16×10^{-3} mol in 200 mL or 0.2 L solution

$$\therefore \quad [KCl] = \frac{16 \times 10^{-3}}{0.2\ L} = 0.08\ M$$

2. **(c) :** $CH_3-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-NH_2 \longrightarrow CH_3-\underset{sp}{C}\equiv N$

3. **(c) :** AsF_5 has sp^3d hybridisation with trigonal bipyramid geometry in which one 'd_{z^2}' one 's' and three 'p' orbitals are involved.

4. **(a) :** $Mg_2C_3 + 4H_2O \longrightarrow \underset{\text{Propyne}}{CH_3-C\equiv CH}$



It has two σ and two π bonds.

5. **(a) :** % ratio of C : H = 6 : 1 and C : O = 3 : 4

$\therefore$ % at. wt. ratio of C : H : O = 6 : 1 : 8

$$\therefore \ \%\ C = \frac{6}{15} \times 100 = 40, \qquad \frac{40}{12} = 3.33$$
$$\%\ H = \frac{1}{15} \times 100 = 6.66, \qquad \frac{6.66}{1} = 6.66$$
$$\%\ O = \frac{8}{15} \times 100 = 53.3, \qquad \frac{53.3}{16} = 3.33$$

$\therefore$ Simplest ratio of C : H : O = 1 : 2 : 1

i.e., CH_2O so, the compound is HCHO.

6. **(c) :** $NaHCO_3$ is acidic and decomposed by NaOH forming Na_2CO_3

$$\underset{\text{Acid}}{NaHCO_3} + \underset{\text{Base}}{NaOH} \rightarrow Na_2CO_3 + H_2O$$

7. **(a)**

8. **(b) :**

	$N_2O_{4(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$
Initial	1		0
At equilibrium	(1 – 0.2)		2 × 0.2

Total moles at equilibrium = (1 – 0.2 + 0.4) = 1.2

$$pV = nRT$$
$$\frac{p_2V_2}{p_1V_1} = \frac{n_2RT_2}{n_1RT_1}$$
$$\frac{p_2 \times V}{1 \times V} = \frac{1.2 \times R \times 600}{1 \times R \times 300}$$
$$p_2 = 2.4\ \text{atm}$$

9. **(b)** **10.** **(d)**

11. **(b) :** Energy of electron in the n^{th} orbit of H-atom is, $E_n = -\frac{13.6}{n^2}$ eV

$\therefore \ E_1 = -13.6$ eV (as $n = 1$)

After absorbing 12.1 eV, the energy will be
= – 13.6 eV + 12.1 eV = – 1.5 eV

Thus, $-\frac{13.6}{n^2} = -1.5\ \text{eV} \ \Rightarrow \ n^2 = 9$ or $n = 3$

Thus, electron will jump to III orbit.

12. (c) : Elements with atomic no. 17 (Cl) and 53 (I) are present in the same group.

13. (b) : Given density of formic acid = 1.22 g cm^{-3}

$\therefore$ Weight of formic acid in 1 litre solution

$= 1.22 \times 10^3$ g

Thus, $[HCOOH] = \frac{1.22 \times 10^3}{46} = 26.5$ M

Since in case of auto-ionisation,

$[HCOOH_2^+] = [HCOO^-]$ and

$[HCOO^-][HCOOH_2^+] = 10^{-6}$

$[HCOO^-] = 10^{-3}$

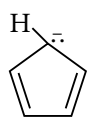
Now, % dissociation of HCOOH

$$= \frac{[HCOO^-]}{[HCOOH]} \times 100 = \frac{10^{-3}}{26.5} \times 100 = 0.004\ \%$$

14. (c)

15. (c) : Le Chatelier's principle makes a qualitative prediction about the effects of change in conditions on equilibrium. Only manufacture of H_2SO_4 (Contact process) involves reversible reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$.

16. (c) :



Cyclopentadienyl anion (planar)
$(C_5H_5)^-$, 6π-electrons
(aromatic)

17. (a)

18. (a) : '*A*' decolourises MnO_4^-/H^+ thus, '*A*' is CaC_2O_4.

$$\underset{(A)}{CaC_2O_4} \rightarrow \underset{(B)}{CO} + \underset{(C)}{CO_2} + \underset{(D)}{CaO}$$

'*B*' burns with blue flame.

$$\underset{(D)}{CaO} + H_2O \rightarrow \underset{(E)}{Ca(OH)_2}$$

$$\underset{(E)}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

19. (c)

20. (a) : Smaller the size of cation, larger is the degree of hydration, hence, larger is the stability of hydrated ion.

21. (b, c, d) **22. (a, b, c)**

23. (a, c) : van der Waals equation is given as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

At large molar volumes,

$$P + \frac{a}{V_m^2} \approx P \text{ and } V_m - b \approx V_m$$

thus, behaves as an ideal gas and van der Waals coefficients a and b are dependent upon the nature of gas.

24. (a, b, c, d)

25. (b, c, d) : *E* and *F*; and also *E* and *G* differ in position of atom (H), so these are tautomers (not resonating structures). *F* and *G* are geometrical isomers. Geometrical isomers are also diastereomers.

26. (d) **27. (c)** **28. (b)**

29. (b) : Work done $= -P_{ext} \times \Delta V = -3(6 - 4)$ L atm $= -6$ L atm $= -6 \times 101.3$ J $= -608$ J

30. (b) : $P_{ext} = 0 \therefore W = -P_{ext}\Delta V = 0$

For adiabatic process, $q = 0 \therefore \Delta U = W = 0$

For ideal gas, $U = f(T)$

As $dU = 0, \therefore dT = 0$

$dH = d(U + PV) = dU + d(RT)$

$= dU + RdT = 0 + 0 = 0$

For isothermal process,

$$\Delta S_T = R \ln \frac{V_2}{V_1} \neq 0$$

31. (d) : The given diagram represents isothermal expansion of the ideal gas from pressure 2.0 atm to 1.0 atm at 298 K.

$$w = -2.303\ nRT\ \log \frac{P_1}{P_2}$$

$$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J } K^{-1}mol^{-1} \times 298 \text{ K} \times \log \frac{2}{1}$$

$= -2.303 \times 8.314 \times 298 \times 0.3010$ J

$= -1717.46$ J

32. (b) **33. (a)** **34. (c)** **35. (b)**

36. (b) : In helium atom (small in size), the intermolecular forces of attraction can be neglected, so that van der Waals equation becomes $P(V - b) = RT$ or $PV = RT + Pb$.

37. (d) : The O—O bond length in H_2O_2 is longer than in O_2F_2 and H_2O_2 is a covalent compound.

38. (b) : Glycerol decomposes at its normal boiling point.

39. (d) : Singlet carbene has a bent structure and the carbon is sp^2 hybridised.

40. (a)

41. (9) : Given, $C_v = 2.5 \text{ kJ K}^{-1} = 2500 \text{ J K}^{-1}$

$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45 \text{ K}$

ΔH due to combustion of 3.5 g of gas

$= C_v \times \Delta T$

$= 2500 \times 0.45 = 1125 \text{ J}$

Given, molecular weight of gas = 28

1 mol of gas = 28 g

Hence, ΔH due to combustion of 1 mole of gas

$$= \frac{1125}{3.5} \times 28 = 9000 \text{ J mol}^{-1}$$

$\therefore$ ΔH in kJ $\text{mol}^{-1} = 9 \text{ kJ mol}^{-1}$

42. (8) : In a 4 : 1 molar ratio of He and CH_4, the partial pressure of He $= \frac{4}{5} \times 10 = 8$ atm

and the partial pressure of CH_4

$$= \frac{1}{5} \times 10 = 2 \text{ atm}$$

According to Graham's law of effusion,

$$\frac{r_{He}}{r_{CH_4}} = \frac{P_{He}}{P_{CH_4}} \times \sqrt{\frac{M_{CH_4}}{M_{He}}} = \frac{8}{2} \times \sqrt{\frac{16}{4}} = 8:1 = 8$$

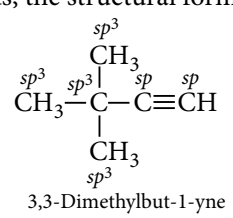
43. (0) :

$W(C_6H_{10})$ —$AgNO_3/NH_4OH$→ white ppt. indicates the presence of triple bond at the terminal position

W —(Hot alkaline $KMnO_4$, [O])→ $(CH_3)_3C-COOH$

2,2-Dimethylpropanoic acid

Thus, the structural formula of W is



3,3-Dimethylbut-1-yne

44. (4) : Let the structure of silver salt of alkyne be

$R-C\equiv C-Ag$

The mass of silver salt which contains 108 g of Ag $= \frac{100}{67.08} \times 108 = 161.0$

Thus, $R + 12 + 12 + 108 = 161$

$R = 29$ or $R = C_2H_5$

So, number of carbon atoms in alkyne = 4.

45. (4) : $PO_4^{3-} \rightarrow x + 4(-2) = -3, \Rightarrow x = +5$

$H_2S_2O_8 \rightarrow 2(+1) + 2x + 2(-1) + 6(-2) = 0$

$\Rightarrow$ $x = +6$ (two oxygen atoms with peroxide linkage).

$H_2SO_5 \rightarrow 2(+1) + x + 2(-1) + 3(-2) = 0$

$\Rightarrow$ $x = +6$ (two oxygen atoms with peroxide linkage).

$OF_2 \rightarrow x + 2(-1) = 0, \Rightarrow x = +2$

$Cr_2O_7^{2-} \rightarrow 2x + 7(-2) = -2, \Rightarrow x = +6$

$CrO_5 \rightarrow x + 4(-1) + (-2) = 0, \Rightarrow x = +6$

(four oxygen atoms with peroxide linkage).

46. (1) : $Cl_2 + \underset{\text{(cold, dil.)}}{2NaOH} \longrightarrow \underset{(X)}{NaCl} + \underset{(Y)}{NaClO} + H_2O$

$3Cl_2 + \underset{\text{(hot)}}{6NaOH} \longrightarrow \underset{(X)}{5NaCl} + \underset{(Z)}{NaClO_3} + 3H_2O$

In Y, *i.e.*, NaClO, the cation is Na^+,

$\therefore$ The oxidation state of Na is +1.

47. (5) : The exceptional outer electronic configuration suggests that the expected configuration of X is $4d^8\ 5s^2$. Thus it belongs to 5^{th} period.

48. (5) : $\upsilon = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{1285 \times 10^{-9} \text{ m}}$

$$= 3.29 \times 10^{15} \left(\frac{1}{3^3} - \frac{1}{n^2} \right)$$

or, $$\frac{1}{n^2} = \frac{1}{9} - \frac{3.0 \times 10^8}{1285 \times 10^{-9}} \times \frac{1}{3.29 \times 10^{15}}$$

$$= 0.111 - 0.071 = 0.04 = \frac{1}{25}$$

or $n^2 = 25$ or $n = 5$.

49. (2) : Pb^{2+} + excess NaOH $\longrightarrow$ $\underset{(Y)\text{ soluble}}{[Pb(OH)_4]^{2-}}$ —H_2O_2→ $\overset{+4}{PbO_2}$ (Z) black ppt.

50. (3) :

	$NO_{2(g)}$	+ $CO_{(g)}$	⇌ $NO_{(g)}$	+ $CO_{2(g)}$
Initial moles	1	2	0	0
At equil.	(1–0.5)	(2–0.5)	0.5	0.5

At equilibrium 0.5 mole of $CO_{(g)}$ was reacted. As volume of the reaction vessel is one litre, so at equilibrium,

$[NO_2] = 0.5$ M, $[CO] = 1.5$ M

$[NO] = [CO_2] = 0.5$ M

$$\Rightarrow \quad K_c = \frac{[NO][CO_2]}{[NO_2][CO]} = \frac{0.5 \times 0.5}{0.5 \times 1.5} = \frac{1}{3}$$

YOU ASKED WE ANSWERED

Do you have a question that you just can't get answered?

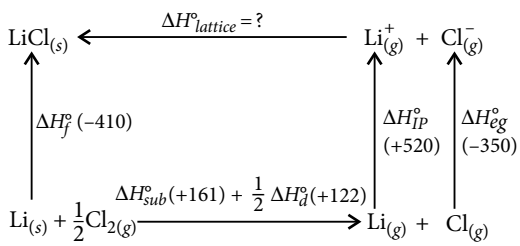
Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. Establish Born-Haber cycle for LiCl crystal and also calculate lattice energy with the help of Born-Haber cycle.

– Parth Savaliya

Ans. Born-Haber cycle for LiCl is shown as :



(Enthalpy changes are given in kJ mol^{-1})

$$\Delta H^\circ_f = \Delta H^\circ_{sub} + \frac{1}{2}\Delta H^\circ_d + \Delta H^\circ_{IP} + \Delta H^\circ_{eg} + \Delta H^\circ_{lattice}$$

$$-410 = +161 + 122 + 520 + (-350) + \Delta H^\circ_{lattice}$$

$$\Delta H^\circ_{lattice} = -863 \text{ kJ mol}^{-1}$$

Q2. What is pyroligneous acid?

– Rehan Rizvi, Vaishali, Bihar

Ans. Pyroligneous acid, also called wood vinegar, is the crude condensate produced from the distillation of smoke generated in the process of making charcoal. The word 'pyroligneous' comes from 'pyrolysis' involving wood and 'lignin' as one of the components in wood.

Physical properties of pyroligneous acid are

Physical properties	Values
Appearance	Reddish brown liquid
Acidity (pH)	2–3
Viscosity (cSt)	20–100 at 40°C
Boiling curve	Starts boiling below 100°C
Auto ignition temperature	Approximately above 500°C
Specific gravity (g/mL)	1.070–1.090 at 25°C
Vapour pressure	Similar to water
Odour	Pleasant-smoky aroma

Chemically, pyroligneous acid consists of a water, water-soluble organic compounds and water-insoluble organic compounds.

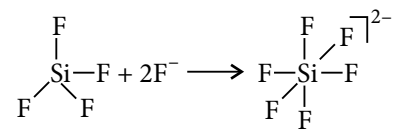
The principal components of pyroligneous acid are acetic acid, acetone and methanol. It was once used as a commercial source for acetic acid. In addition, the 'wood vinegar' often contains 80-90% water along with some 200 organic compounds. Some important applications of pyroligneous acid are in the field of agriculture, swine and poultry culture and floriculture.

Q3. Why is $SiCl_4$ a weaker Lewis acid than SiF_4?

– Rajat Gupta, Mumbai

Ans. Unlike carbon, silicon atom being large in size can expand its covalency beyond 4.

Lewis acid-base reaction of SiF_4 with two F^- ions is shown as :



Acidic strength increases in the order :

$SiI_4 < SiBr_4 < SiCl_4 < SiF_4$

due to increase in the electron-withdrawing power of the halogen from I to F.

This order is reverse of that for BX_3.

CONCEPT BOOSTER

Dear students, this is the last part of *p*-block elements. Hope you will enjoy reading it. Wish you all a very happy new year. Stay well, keep yourself healthy. Take care!!

*Arunava Sarkar

Important Reactions of SO_2

SO_2 is both oxidising and reducing in nature. Because in SO_2, oxidation state of sulphur is +4 and it can either increase or decrease it. Here are some important reactions which depict both oxidising and reducing nature of SO_2.

In SO_2, sulphur has an oxidation number of +4 which can either decrease (mainly $\overset{0}{S}$, S(in $H_2\overset{-2}{S}$)) or increase ($H_2\overset{+6}{S}O_4$). So, SO_2 can act both as oxidising and reducing agent.

Reducing Nature of SO_2

$$SO_{2(g)} + 2H_2O_{(l)} \longrightarrow H_2SO_4 + 2[H]$$

This nascent hydrogen is responsible for the reducing property of SO_2. Moreover, this is also responsible for the bleaching action of SO_2.

Coloured substance +[H] $\longrightarrow$ Decolourised

However, this bleaching is temporary as when the decolourised substance is kept in open air, it gets oxidised and gains its previous colour infact its own colour.

How SO_2 carries out the reduction process?

Example 1 : SO_2 is passed through Cl_2 water.

1. $Cl_2 + H_2O \longrightarrow HCl + HOCl$
2. $HOCl \longrightarrow HCl + [O]$
3. $SO_2 + [O] + H_2O \longrightarrow H_2SO_4$

Where is the use of nascent hydrogen? How is it showing the reducing property of SO_2?

SO_2 is oxidised. Where does this nascent oxygen come from? From Cl_2? Yes, so, Cl_2 is reduced!!

It is in fact an indirect way of reduction. This is also believed to occur.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$
$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

A possible combination

From the previous demonstration,

(1) + (2) + (3) $\Rightarrow$

$$Cl_2 + SO_2 + 2H_2O \longrightarrow \underbrace{2HCl + H_2SO_4}_{\text{Two products are both acids}}$$

This is an example where both the products are acids.

Example 2 : SO_2 is passed through acidified $KMnO_4$ solution.

Now first objective is to produce nascent oxygen.

1. $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
2. $SO_2 + H_2O + [O] \longrightarrow H_2SO_4$

(1) + [(2) × 5] $\Rightarrow$

$$\underset{\text{Pink violet}}{2\overset{+7}{K}\overset{+7}{M}nO_4} + 5\overset{+4}{S}O_2 + 2H_2O \longrightarrow K_2SO_4 + \underset{\text{Colourless}}{2\overset{+2}{M}nSO_4} + 2H_2\overset{+6}{S}O_4$$

There is a notable point here that though it is said that 'acidified $KMnO_4$ solution' but at the final balanced reaction there is no acid at the left hand side. Why is this?

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

Example 3 : In the similar fashion, it is said that the orange colour of $K_2Cr_2O_7$ is decolourised when SO_2 is passed through it.

$$\underset{\text{Orange}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

Example 4 : What happens when SO_2 is passed through ferric sulphate solution?

Now, here a little bit change in the strategy is required. As the salt already contains sulphate unit so its reaction with H_2SO_4 cannot be written. So here direct and normal reduction process is required.

1. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$
2. $Fe_2(SO_4)_3 + 2[H] \longrightarrow 2FeSO_4 + H_2SO_4$

(1) + (2) ⇒

$$SO_2 + Fe_2(SO_4)_3 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

Oxidising Nature of SO_2

As already said, SO_2 is oxidising in nature also.

The following reactions demonstrate that.

1. $\overset{+4}{SO_2} + 2\overset{-2}{H_2S} \longrightarrow 2H_2O + \overset{0}{3S}\downarrow$

   Oxidation; Reduction

2. When SO_2 is passed through $SnCl_2$ solution added with dil. HCl, then $SnCl_4$ is produced.

   $$\overset{+2}{2SnCl_2} + 4HCl + SO_2 \longrightarrow \overset{+4}{2SnCl_4} + 2H_2O + S$$

3. $$\overset{0}{4K} + \overset{+4}{3SO_2} \longrightarrow \overset{+1}{K_2SO_3} + \overset{+2}{K_2S_2O_3}$$

   $$\overset{0}{3Fe} + \overset{+4}{SO_2} \longrightarrow \overset{+2}{2FeO} + \overset{+2\ -2}{FeS}$$

Add to Your Knowledge

What happens when in the potassium iodate solution SO_2 gas is passed?

Ans.: 1. $2KIO_3 + 5SO_2 + 4H_2O \longrightarrow 2KHSO_4 + I_2 + 3H_2SO_4$

2. $I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$

(1) + (2) ⇒

$$2KIO_3 + 6SO_2 + 6H_2O \longrightarrow 2HI + 4H_2SO_4 + 2KHSO_4$$

What happens when SO_2 is passed through lime water?

Ans.: $SO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Insoluble in water}}{CaSO_3}\downarrow + H_2O$

$$CaSO_3 + H_2O + SO_2 \longrightarrow \underset{\text{Soluble in water}}{Ca(HSO_3)_2}$$

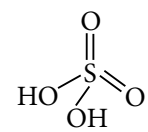
- **Addition reactions of SO_2:**
  - $SO_2 + Cl_2 \xrightarrow{\text{charcoal}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$
  - $SO_2 + PCl_5 \longrightarrow \underset{\text{Thionyl chloride}}{SOCl_2} + \underset{\text{Phosphoryl chloride}}{POCl_3}$

Oxoacids of Sulphur

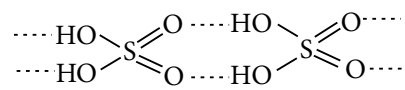
As obvious, the most important is H_2SO_4. Industrially H_2SO_4 is prepared through Contact process. Look at the following aspects :

- Optimum temperature → 720 K
- Optimum pressure → 2 bar
- Removal of impurities

Structure of H_2SO_4 is as follows :



and it also shows H-bonding in between the molecules :



This is why H_2SO_4 has high density and high boiling point.

H_2SO_4 is a strong oxidising agent. For example,

$$H_2SO_4 \xrightarrow{\Delta} H_2O + SO_2 + [O]$$

$$C + 2[O] \longrightarrow CO_2$$

Some Important Reactions of H_2SO_4

1. (i) $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$

   (ii) $HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$

   (iii) $C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$

   All the above reactions depict that H_2SO_4 is a dehydrating agent.

2. (i) $K_4[Fe(CN)_6] + 3H_2SO_4(dil.) \longrightarrow 2K_2SO_4 + FeSO_4 + 6HCN$

(ii) $K_4[Fe(CN)_6] + 6H_2SO_4\ (conc.) + 6H_2O \longrightarrow 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$

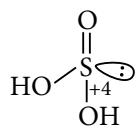
Add to Your Knowledge

- $K_4[Fe(CN)_6] \xrightarrow{\Delta} FeC_2 + 4KCN + N_2$
- $K_4[Fe(CN)_6] \xrightarrow{\text{strong } \Delta} Fe + 4KCN + \underset{\text{Pseudo halogen}}{(CN)_2}$
- $3KClO_3 + 3H_2SO_4 \xrightarrow{\Delta} 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

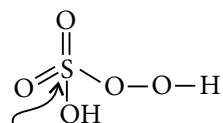
Structures of other oxoacids can be drawn with the following strategy :

- With S atom put a single bonded —OH group and double bonded oxygen at first.
- Then, if required increase =O group as well as —OH group.
- Check the oxidation number obtained through the calculation with that obtained through the structure.

- **H_2SO_3 :**

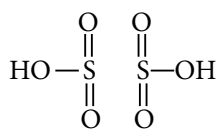


- **H_2SO_5 :**



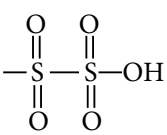
It won't be +8. See here

- **$H_2S_2O_6$:**



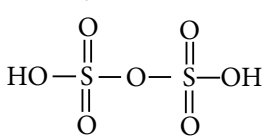
Step 1

No more 'O' left.

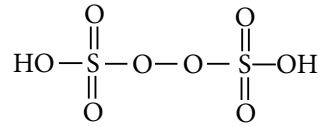
Therefore, 

Step 2

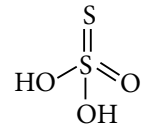
- **$H_2S_2O_7$:** From the above structure



- **$H_2S_2O_8$:** Same logic.



Exception to the above strategy will be $H_2S_2O_3$ which is



[This can also be anticipated as the normal strategy will violate symmetry.]

GROUP 17 ELEMENTS

Some common sources of halogen elements :

Fluorine

- Cryolite : Na_3AlF_6
- Fluorspar : CaF_2
- Fluorapatite : $CaF_2{\cdot}3Ca_3(PO_4)_2$

Chlorine

- Rock salt : NaCl
- Carnallite : $KCl{\cdot}MgCl_2{\cdot}6H_2O$

Bromine

- From NaBr, KBr of sea water

Iodine

- Coppice under the sea (some algaes infact)
- Caliche or chile saltpetre which is mainly sodium nitrate containing iodine in the form of sodium iodate ($NaIO_3$). Amount of iodine present is very less, nearly 0.2%.

'*Halogen*' means *salt forming elements* or *salt formers*. '*Halo*' = *sea salts*, '*genes*' = *producing*. Halogens are quite reactive, fluorine being the most reactive is called '*super halogen*'. Fluorine is thirteenth most abundant element on the earth's crust. Astatine (At) is that halogen which is radioactive in nature.

In general, colour of the halogen elements :

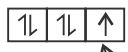
- F_2 gas is light yellow.
- Cl_2 gas is yellow-green.
- Br_2 (both in gaseous and liquid state) is dark red brown.
- I_2 (gas) is violet. I_2 (solid) is black.

Different colours are due to absorption of different wavelengths of light and promotion of electron to different energy levels.

Different Oxidation States

Fluorine does not have vacant *d*-orbitals, it cannot extend its oxidation state. It only shows –1 oxidation state.

$F(9) \rightarrow 1s^2, 2s^2, 2p^5$

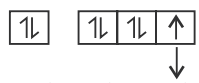


Only can accept here.
No tendency of loosing electrons.

However, for the other members (except astatine) the available oxidation states are (available to each of them) : –1, +1, +3, +5, +7.

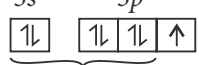
–1 is of course the main oxidation state.

$Cl(17) \rightarrow {}_{10}[Ne]\ 3s^2\ 3p^5$ (+1)

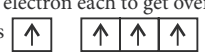


Releases this one electron to get + 1.

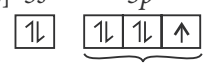
$Cl(17) \rightarrow {}_{10}[Ne]\ 3s^2\ 3p^5$ (+3)



Releases one one electron each to get overall half-filled state as

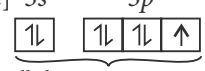


$Cl(17) \rightarrow {}_{10}[Ne]\ 3s^2\ 3p^5$ (+5)



Releases all five electrons to get stable ns^2 (*i.e.* $3s^2$ here) state.

$Cl(17) \rightarrow {}_{10}[Ne]\ 3s^2\ 3p^5$ (+7)



Releases all electrons to get nearest noble gas/fully-filled electronic configuration.

Few important points regarding some common properties of halogen elements :

- Ionization enthalpy order is : F > Cl > Br > I
- Electron gain enthalpy order is as follows :
  Cl (–349) > F (–333) > Br (–325) > I (–296)
  Order is according to the more negative to less negative.
- With the increase in the size, van der Waals force of attraction increases which results into the increase in melting and boiling points from fluorine to iodine. This is pertinent to say that at normal temperature, F_2 and Cl_2 are gases whereas Br_2 is liquid and I_2 is solid.
- Enthalpy of bond dissociation : Due to smaller size, fluorine atoms in F_2 molecule experience greater amount of repulsion force which naturally helps to dissociate the bond between fluorine atoms. Overall order is : $Cl_2 > Br_2 > F_2 > I_2$.
- Halogens are coloured. They absorb the energy of a certain wavelength and release its complementary colour.
  For example, fluorine, due to absorption of violet light emits pale yellow. Reverse is true for I_2. For the similar kind of reason, Br_2 is reddish brown and Cl_2 is greenish yellow.

Chemical Reactivity in the Light of Oxidising Power

Halogens are electronegative and hence oxidising in nature. Fluorine being the most electronegative is the most oxidising indeed. Overall the anion formation process for halogens is as below :

$$\frac{1}{2}X_{2(g)} \xrightarrow{\frac{1}{2}\Delta_{BD}H^\circ} X_{(g)} \xrightarrow{\Delta_{eg}H^\circ} X^-_{(g)}$$

(*BD* = Bond Dissociation)

and in aqueous solution, finally

$$X^-_{(g)} \xrightarrow{\Delta_{hyd}H^\circ} X^-_{(aq)}$$

Fluorine has large negative value of $\Delta_{hyd}H^\circ$ as it is strongest H-bonding forming agent. Moreover, standard reduction potential values of the halogens are as below :

$F_2 + 2e^- \rightarrow 2F^-$; $E^\circ = +2.87$ V
$Cl_2 + 2e^- \rightarrow 2Cl^-$; $E^\circ = +1.36$ V
$Br_2 + 2e^- \rightarrow 2Br^-$; $E^\circ = +1.09$ V
$I_2 + 2e^- \rightarrow 2I^-$; $E^\circ = +0.54$ V

Some Common Evidences of Oxidising Power of Halogens

F_2

- It oxidises even oxygen.

$$F_2 + \underset{\text{liquid air}}{O_2} \xrightarrow[\text{low pressure}]{\text{electric discharge}} \overset{+1}{O_2F_2}$$

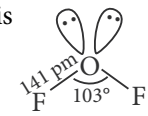
- F_2 reacts with water to give O_2 and O_3 both.

$$2F_{2\,(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$
$$\{4H^+_{(aq)} + 4F^-_{(aq)}\}$$
$$3F_{2(g)} + 3H_2O_{(l)} \longrightarrow O_{3(g)} + 6HF_{(aq)}$$
$$\{6H^+_{(aq)} + 6F^-_{(aq)}\}$$

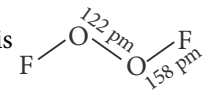
❍ $\overset{0}{2F_{2(g)}} + 2\underset{(2\%)}{\overset{-2}{NaOH}} \longrightarrow 2\overset{-1}{NaF} + H_2O + \overset{+2}{OF_2}$

OF_2 is known as *oxygen difluoride*. Here, oxygen atom is sp^3 hybridised.

Structure is



Structure of O_2F_2 is



O_2F_2 is known as *dioxygen difluoride*. O_2F_2 is quite unstable. However, both OF_2 and O_2F_2 can be used as strong fluorinating agents.

Cl_2

Cl_2 is oxidising because in its aqueous solution, it can generate nascent oxygen.

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

Hypochlorous acid

$HOCl \longrightarrow HCl + [O]$

This nascent oxygen is responsible for the oxidising power as well as bleaching action of Cl_2. Few examples showing the oxidising properties of Cl_2 :

Example 1 : $Cl_2 + H_2O \longrightarrow 2HCl + [O]$ ... (1)

$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$

(1) + (2) $\Rightarrow$ ... (2)

$2FeSO_4 + Cl_2 + H_2SO_4 \longrightarrow 2HCl + Fe_2(SO_4)_3$

Example 2 : $Cl_2 + H_2O \longrightarrow 2HCl + [O]$ ... (1)

$I_2 + 5[O] \longrightarrow I_2O_5$ ... (2)

$I_2O_5 + H_2O \longrightarrow 2HIO_3$ ... (3)

$[(1)\times 5] + (2) + (3) \Rightarrow$

$5Cl_2 + 5H_2O + I_2 + 5[O] + I_2O_5 + H_2O \longrightarrow 10HCl + 5[O] + I_2O_5 + 2HIO_3$

$\Rightarrow 5Cl_2 + I_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$

After this, in case of Br_2 or I_2, oxidising power is highly reduced.

Reaction between Br_2 and H_2O is still possible as shown below :

$Br_2 + H_2O \longrightarrow 2HBr + [O]$

But the reaction between I_2 and H_2O is non-spontaneous and in acidic solution rather, reverse reaction is found to occur.

$4I^-_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \not\rightleftharpoons 2I_{2(s)} + 2H_2O_{(l)}$

Preparation

F_2

Preparation of F_2 is not that easy due to its unconventional behaviour. However, following methods are there in order to prepare fluorine.

❍ Moissan method

❍ Dennis method

❍ Whytlaw and Gray method

Moissan Method

❍ **Electrolytic cell :** Electrolytic cell here is a U-tube made of Pt-Ir alloy. Two mouths of the U-tube is closed with two corks made of fluorspar (CaF_2). Through these mouths, electrodes made of Pt-Ir alloy again, are inserted through the cork.

❍ **Electrolyte :** KHF_2 dissolved in anhydrous HF.

❍ **Reactions involved :**

$HF + KF \longrightarrow KHF_2$

$KHF_2 \rightleftharpoons K^+ + HF_2^-$

$HF_2^- \rightleftharpoons HF + F^-$

Cathode reactions : $2K^+ + 2e^- \rightleftharpoons 2K$

$2K + 2HF_2^- \longrightarrow 2KF + H_2\uparrow + 2F^-$

Anode reaction : $2F^- \longrightarrow F_2 + 2e^-$

Overall : $2KHF_{2(l)} \longrightarrow F_{2(g)} + H_{2(g)} + 2KF$

Q. What happens when in cold NaOH solution, F_2 gas is passed?

Ans.: In the cold, aqueous NaOH if F_2 gas is passed, then OF_2 is produced.

$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$

Now, in OF_2, oxidation number of oxygen is +2. It is a powerful oxidising agent. When OF_2 reacts with water at normal temperature, it gives HF and O_2.

Oxidation

$\overset{+2}{OF_2} + H_2\overset{-2}{O} \longrightarrow \overset{0}{O_2} + 2HF$

Reduction

Here, both O^{2+} and O^{2-} go to $\overset{0}{O_2}$. This reaction is known as **comproportionation reaction**.

Q. Prove that, oxidising power of F_2 is more than (i) $KClO_3$, (ii) K_2SO_4, and (iii) K_2CO_3.

Ans.:

(i) $\overset{+5}{KClO_3} + \overset{0}{F_2} + H_2O \longrightarrow \overset{+7}{KClO_4} + 2\overset{-1}{HF}$

Potassium perchlorate

(ii) $2\overset{+6}{K_2SO_4} + \overset{0}{F_2} \longrightarrow \underset{\text{Potassium persulphate}}{\overset{+7}{K_2S_2O_8}} + 2\overset{-1}{KF}$

(iii) $2\overset{+4}{K_2CO_3} + F_2 \longrightarrow \underset{\text{Potassium percarbonate}}{\overset{+5}{K_2C_2O_6}} + 2\overset{-1}{KF}$

Q. What happens when NH_4F is heated?

Ans.: $2NH_4F \longrightarrow NH_3 + \underset{\text{Ammonium hydrogenfluoride}}{(NH_4)HF_2}$

Q. How can you identify fluoride salt?

Ans.: Fluoride salt $\xrightarrow[\Delta]{SiO_2/\text{conc. } H_2SO_4} SiF_{4(g)}$

If a platinum wire with a drop of water at its tip, is held in the silicon tetrafluoride gas, then the water drop becomes opaque as wax and this is due to the production of solid silicic acid.

e.g., $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$

$3SiF_4 + 4H_2O \longrightarrow \underset{\text{Hydrofluorosilicic acid}}{2H_2SiF_6} + Si(OH)_4$

Q. Why the bond dissociation energy of F_2 is only 36 kcal mol^{-1}?

Ans.: Size of fluorine atom is very small. F_2 molecule has a covalent radius of 64 pm. This is why the lone pairs of fluorine atoms strongly repel each other and make the F — F bond quite weak.

Preparation

Cl_2

In the laboratory, mixture of conc. HCl and MnO_2 is heated to give Cl_2 gas.

1. $2MnO_2 + 8HCl \longrightarrow 2MnCl_3 + Cl_2 + 4H_2O$
2. $2MnCl_3 \longrightarrow 2MnCl_2 + Cl_2$

(1) + (2) $\Rightarrow$

$2MnO_2 + 8HCl \longrightarrow 2MnCl_2 + 2Cl_2 + 4H_2O$

$\Rightarrow MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Produced Cl_2 has some water vapours and HCl gas in it. At first it is passed through water so that HCl vapours get dissolved and then passed through conc. H_2SO_4 to dry it.

Q. How can you get Cl_2 gas at ordinary temperature?

Ans.: In a conical flask $KMnO_4$ crystal is taken and dropwise conc. HCl is added into it. Cl_2 gas is produced.

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$

Q. What happens when a mixture of NaCl, MnO_2 and conc. H_2SO_4 is heated?

Ans.: $2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$

$MnO_2 + H_2SO_4 + 2HCl \longrightarrow MnSO_4 + Cl_2\uparrow + 2H_2O$

$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + Cl_2\uparrow + 2H_2O$

Q. What do you mean by 'available chlorine' from bleaching powder?

Ans.: Bleaching powder is Ca(OCl)Cl. When bleaching powder reacts with HCl then we get chlorine from it. From a 100 part (as per weight) sample of bleaching powder, part of chlorine (as per weight) that is obtained is known as available chlorine. In general, commercially available bleaching powder has 35% or 37% as available chlorine.

Q. What happens when chlorine reacts with
(i) dilute and cold NaOH
(ii) conc. and hot NaOH?

Ans.: (i) Dilute and cold NaOH reacts with Cl_2 to give NaCl and NaOCl.

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

(ii) Conc. and hot NaOH reacts with Cl_2 to give NaCl and $NaClO_3$ (sodium chlorate).

$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

Q. What happens when chlorine reacts with
(i) lime water, (ii) hot lime, (iii) dry lime, (iv) white hot lime?

Ans.: (i) $2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\substack{\text{Calcium}\\\text{hypochlorite}}}{CaCl_2 + Ca(OCl)_2} + 2H_2O$

(ii) $6Ca(OH)_2 + 6Cl_2 \longrightarrow \underset{\substack{\text{Calcium}\\\text{chlorate}}}{5CaCl_2 + Ca(ClO_3)_2} + 6H_2O$

(iii) $\underset{\text{(dry)}}{Ca(OH)_2} + Cl_2 \xrightarrow{40°C\text{-}50°C} Ca(OCl)Cl + H_2O$

(iv) $2CaO + 2Cl_2 \longrightarrow 2CaCl_2 + O_2\uparrow$

Q. What happens when chlorine reacts with
(i) little amount of NH_3
(ii) large amount of NH_3?

Ans.: (i) With little amount of NH_3, an explosive liquid NCl_3 is produced.

$$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl\uparrow$$

(ii) With large amount of NH_3, ammonium chloride and N_2 are produced.

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2\uparrow$$

Q. What happens when dry chlorine gas is passed over slightly hot silver nitrate?

Ans.: In the reaction, white silver chloride, nitrogen pentoxide and O_2 gas are produced.

$$4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl + 2N_2O_5 + O_2$$

Q. What happens when the mixture of calcium phosphate and carbon is heated with CO and Cl_2?

Ans.: $$Ca_3(PO_4)_2 + 6CO + 6Cl_2 \xrightarrow{300°C} 3CaCl_2 + 2POCl_3 + 6CO_2$$

Q. What happens when excess Cl_2 is passed through the iodine suspended in water?

Ans.: Here, iodine is oxidised to HIO_3 and Cl_2 is reduced to HCl.

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

Q. What happens when Cl_2 is passed through KOH solution?

Ans.: $$3Cl_2 + 6KOH \longrightarrow KClO_3 + 5KCl + 3H_2O$$

Q. What happens when excess amount of silver nitrate is added to the Cl_2 water?

Ans.: $$H_2O + Cl_2 \longrightarrow HCl + HOCl$$

In chlorine water, both hydrochloric acid and hypochlorous acid are present. So, the following observations are there.

(a) HCl will react with $AgNO_3$ to give white ppt. of AgCl.

(b) Excess $AgNO_3$ will react with HOCl to give silver hypochlorite. Silver hypochlorite, in disproportionation reaction gives silver chlorate which is soluble in water.

(c) No amount of Cl_2 gas will remain till the end with the formation of HNO_3, solution will remain acidic.

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$
$$AgNO_3 + HOCl \longrightarrow AgClO + HNO_3$$
$$3AgClO \longrightarrow 2AgCl + AgClO_3$$

Q. What happens when Cl_2 reacts with
(i) Na_2SO_3 (ii) $Na_2S_2O_3$?

Ans.:

(i) $$\overset{+4}{Na_2S}\overset{}{O_3} + \overset{0}{Cl_2} + H_2O \longrightarrow \overset{+6}{Na_2S}\overset{}{O_4} + 2\overset{-1}{H}\overset{}{Cl}$$

(ii) $$\overset{+2}{Na_2S_2}O_3 + 5H_2O + 4\overset{0}{Cl_2} \longrightarrow \overset{+6}{Na_2S}O_4 + H_2SO_4 + 8\overset{-1}{H}Cl$$

Cl_2 is an oxidising agent in both the reactions.

Q. Give an example where Cl_2 is used as a reducing agent.

Ans.: $$\overset{0}{F_2} + \overset{0}{Cl_2} \longrightarrow 2\overset{+1\,-1}{ClF}$$

or $$3\overset{0}{F_2} + \overset{0}{Cl_2} \longrightarrow 2\overset{+3\,-1}{ClF_3}$$

Q. What happens when Cl_2 reacts with
(i) potassium manganate
(ii) potassium ferrocyanide?

Ans.: (i) $$2K_2\overset{+6}{Mn}O_4 + \overset{0}{Cl_2} \longrightarrow 2K\overset{+7}{Mn}O_4 + 2\overset{-1}{K}Cl$$

Solution will turn pink.

(ii) $$2K_4[\overset{+2}{Fe}(CN)_6] + Cl_2 \longrightarrow 2K_3[\overset{+3}{Fe}(CN)_6] + 2KCl$$

Q. What happens when chlorine reacts separately with (i) CO, (ii) NO, (iii) SO_2? Are they oxidation-reduction reactions?

Ans.: (i) $$\overset{+2}{C}O + \overset{0}{Cl_2} \longrightarrow \overset{+4\ -1}{COCl_2}$$

(ii) $$\overset{+2}{N}O + \overset{0}{Cl_2} \longrightarrow 2\overset{+3\ -1}{NOCl}$$

(iii) $$\overset{+4}{SO_2} + \overset{0}{Cl_2} \longrightarrow \overset{+6\ -1}{SO_2Cl_2}$$

All the above reactions are oxidation-reduction as well as addition reactions.

Q. Explain the following observation :
"A wet blue litmus paper turns red at first with Cl_2 but later gets decolourised."

Ans.: $Cl_2 + H_2O \longrightarrow HCl + HOCl$

↓

This helps the blue litmus paper to turn red.

$HOCl \longrightarrow HCl + [O]$

↓

This helps to decolourise.

Q. Convert : $CS_2 \longrightarrow CCl_4$

Ans.: $CS_2 + 3Cl_2 \xrightarrow{I_2} CCl_4 + S_2Cl_2$

Sulphur monochloride

Q. What happens when HCl reacts with $K_2Cr_2O_7$?

Ans.: $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

Q. What happens when aqueous solution of bleaching powder is added to the hot lead acetate solution?

Ans.: $(CH_3COO)_2Pb + Ca(OCl)Cl + H_2O \longrightarrow \underset{\text{Brown}}{PbO_2}\downarrow + 2CH_3COOH + CaCl_2$

Q. In the laboratory, Cl_2 is produced when a mixture of MnO_2 and conc. HCl is heated. Before heating, with the emergence of little Cl_2 a brown colour is also produced. What is that?

Ans.: $2MnO_2 + 8HCl \longrightarrow \underset{\text{Brown}}{2MnCl_3} + Cl_2 + 4H_2O$

$2MnCl_3 \xrightarrow{\Delta} 2MnCl_2 + Cl_2\uparrow$

Br_2

Q. In laboratory, how can you prepare pure Br_2?

Ans.: (1) In retort, take the mixture of KBr, MnO_2 and conc. H_2SO_4. Heat it. Br_2 vapours come out and in contact with the flask get condensed and liquified.

$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow MnSO_4 + 2KHSO_4 + 2H_2O + Br_2\uparrow$

(2) This Br_2 contains the following impurities, (i) water vapours (ii) Cl_2 (iii) I_2.

Now mix KBr and ZnO with liquid Br_2 and heat it.

$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

$2ZnO + 2I_2 \longrightarrow 2ZnI_2 + O_2$

O_2 does not react with Br_2. Use conc. H_2SO_4 to remove water vapours.

Q. How can you prepare Br_2 from carnallite?

Ans.: Though the formula of carnallite is $KCl{\cdot}MgCl_2{\cdot}6H_2O$ but around 1% $MgBr_2$ is present in that. Dissolve carnallite in water and make it dense through heating, KCl precipitates out. Filtering the solution, the filtrate thus obtained contains mainly $MgCl_2$ and $MgBr_2$. This filtrate is known as **Bittern**. Pass Cl_2 through this. Br_2 vapours are produced. These are collected and get converted to liquid form on condensation.

$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2\uparrow$

Q. What happens when Br_2 reacts with
(i) cold, dilute NaOH solution
(ii) hot, conc. NaOH solution?

Ans.: (i) $Br_2 + 2NaOH \longrightarrow NaBr + NaOBr + H_2O$

(ii) $3Br_2 + 6NaOH \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$

Q. Give an example which shows bromine is oxidising in nature.

Ans.: $\overset{-2}{H_2S} + Br_2 \longrightarrow \overset{-1}{2HBr} + \overset{0}{S}\downarrow$

I_2

Q. How can you prepare I_2 in laboratory?

Ans.: $2KI + MnO_2 + 3H_2SO_4 \longrightarrow MnSO_4 + 2KHSO_4 + 2H_2O + I_2$

Q. Give examples of oxidising and reducing nature of I_2.

Ans.: **Oxidising nature :**

$\overset{-2}{H_2S} + \overset{0}{I_2} \longrightarrow \overset{-1}{2HI} + \overset{0}{S}$

Reducing nature :

$\overset{0}{I_2} + 10HNO_3 \longrightarrow \overset{+5}{2HIO_3} + 10NO_2 + 4H_2O$

GROUP 18 ELEMENTS

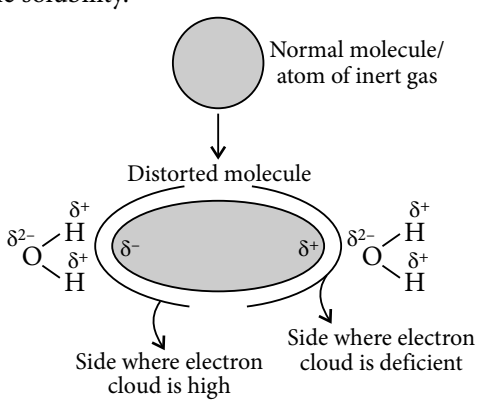
He, Ne, Ar, Kr, Xe and Rn — these are called '*noble gases*'. Earlier they were better known as '*inert gases*' as it was not into the light that though very small, still they can react, at least some of them (like xenon).

A few important points for group 18 elements will be as below :

- They have stable outer electronic configuration as $ns^2\ np^6$. [He has $1s^2$ configuration.]

- They are monatomic in nature as they do not even undergo reactions among themselves.
- Ionisation enthalpy is very high. This is due to the stable electronic configuration. As we move down the group, due to the increase in the atomic radii and thus strong shielding effect, ionisation enthalpy decreases. In kJ mol^{-1} unit, the values of the ionisation enthalpies of noble gases are : He → 2371, Ne → 2080, Ar → 1522, Kr → 1350, Xe → 1169.2, Rn → 1036.
- As noble gases do not form molecules, their van der Waals radii can be calculated which are definitely greater than the covalent radii of the other elements.
- Noble gases have completely filled electronic configuration and thus reluctant to accept electrons. Hence, they have positive electron gain enthalpy.
- As the atoms of the noble gases are held together by weak van der Waals forces, hence they have low melting and boiling points. With the increase in the size of the atoms, extent of van der Waals forces of attraction increases. So, melting and boiling points also increase.
- Though to a very small extent, but inert gases are soluble in water.

  With the increase in the polarisability of the inert gases, solubility increases in water. If the size of the inert gas increases, water or such polar solvent induces dipole moment in it. More will be the dipole induced, more will be the solubility.



Chemical Properties and Chemical Reactions of Noble Gases

It is known that noble gases are chemically inert and they do not show spontaneous reactivity. However, it was found that when xenon is allowed to react with a powerful oxidising agent like PtF_6, it gives the compound $XePtF_6$.

$$Xe + PtF_6 \xrightarrow{278\ K} Xe^+[PtF_6]^-$$

Later on, many other xenon compounds were also prepared like

$$\underset{\text{Excess}}{Xe_{(g)}} + F_{2(g)} \xrightarrow[1\ bar]{395-400^\circ C} XeF_{2(s)}$$

$$\underbrace{Xe_{(g)} + 2F_{2(g)}}_{\text{Ratio 1 : 5}} \xrightarrow[6.5-7\ bar]{600^\circ C} XeF_{4(s)}$$

$$\underbrace{Xe_{(g)} + 3F_{2(g)}}_{\text{Ratio 1 : 18 or 1 : 20}} \xrightarrow[60-70\ bar]{300^\circ C} XeF_{6(s)}$$

When XeF_4 reacts with O_2F_2 at 140-145 K, then also XeF_6 is prepared as below :

$$XeF_4 + O_2F_2 \xrightarrow{140-145\ K} XeF_6 + O_2$$

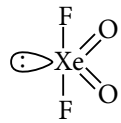
Reactions of Xenon fluorides with Water

- **XeF_2 :** XeF_2 reacts slowly with water to give O_2 and Xe along with HF.
  $2XeF_{2(s)} + 2H_2O_{(l)} \rightarrow 2Xe_{(g)} + 4HF_{(aq)} + O_{2(g)}$
- **XeF_4 :** XeF_4 reacts violently and rapidly with water to give an explosive substance XeO_3 or xenon trioxide.
  $6XeF_{4(s)} + 12H_2O_{(l)} \rightarrow 4Xe_{(g)} + 2XeO_{3(s)} + 24HF_{(aq)} + 3O_{2(g)}$
- **XeF_6 :** XeF_6 in the similar manner, with H_2O reacts violently and gives the explosive solid XeO_3.
  $XeF_{6(s)} + 3H_2O_{(l)} \rightarrow XeO_{3(s)} + 6HF_{(aq)}$

Some Common Structures involving Noble Gases

- **$XeOF_4$:** $8e^-$s of Xe + double bonded O's $2e^-$s + $4e^-$s of F = $14e^-$s = $7e^-$ pairs.
  4σ bp with four F + 1σ bp with O
  $+1\pi$ bp with O → Not considered in hybridisation + 1 lp = sp^3d^2
  Therefore, it will be square pyramidal.
  (AB_5L type)

- **XeO_2F_2 :** $8e^-$s of Xe + $4e^-$s from two double bonded O + $2e^-$s from two F = $14e^-$s = $7e^-$ pairs
  2σ bp with two F + 2σ bp with two O
  + 2π bp with O → Not considered in hybridisation
  + 1 lp = sp^3d
  So, structure will be see-saw (AB_4L) type



[Why fluorine atoms on the axial positions?Follow Bent's rule]

Question from Students' mind

How to find out whether oxygen atoms are double bonded or not?

Ans.: How many valence e^-s in Xe?
No. of valence e^-s in Xe = 8
Now, out of this how many e^-s are given to F.
For example, in $XeOF_4$, for four fluorine atoms we need four electrons.
e^-s given to F = 4
Now, how many left in Xe?
e^-s left in Xe = 4
e^-s required to form double bond in oxygen = 2
As Xe has four e^-s left, then it will form double bond.

Recommended structures for practice

XeO_3, XeO_4, XeO_3F_2, XeO_2F_4, XeF_2, XeF_4, XeF_6, $XeOF_2$.

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UNIT-7

Organic Compounds Containing Oxygen | Organic Compounds Containing Nitrogen

ORGANIC COMPOUNDS CONTAINING OXYGEN

- Preparations, Properties, Reactions and Uses
- Alcohols, Phenols and Ethers
- Aldehydes and Ketones
- Carboxylic Acids

TIPS TO REMEMBER

ALCOHOLS

❑ Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.

❑ In common system, alcohols are named as alkyl alcohols.

❍ In IUPAC system, alcohols are called '*alkanols*', by replacing '*-e*' of alkane by '*-ol*'.

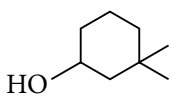
$CH_3-CH_2-CH_2-OH$

Common name : *n*-Propyl alcohol

IUPAC name : Propan-1-ol

SELF CHECK

1. The IUPAC name of the compound

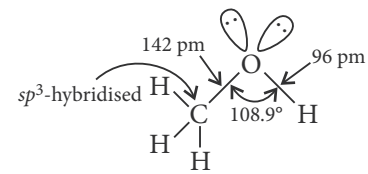


is

(a) 3,3-dimethyl-1-hydroxycyclohexane
(b) 1,1-dimethyl-3-hydroxycyclohexane
(c) 3,3-dimethyl-1-cyclohexanol
(d) 1,1-dimethyl-3-cyclohexanol.

(AIEEE 2004)

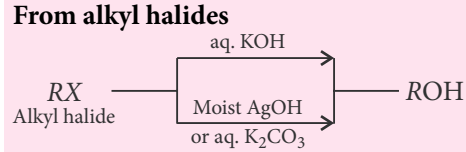
❑ **Structure**



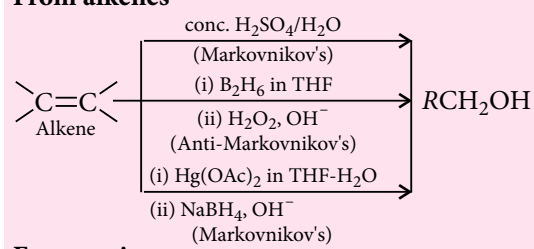
❍ Bond angle is slightly less than tetrahedral angle (109°28′) due to the repulsion between two lone pairs of electrons of O-atom.

❑ **Preparation**

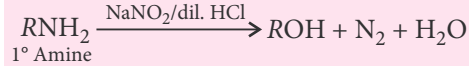
From alkyl halides



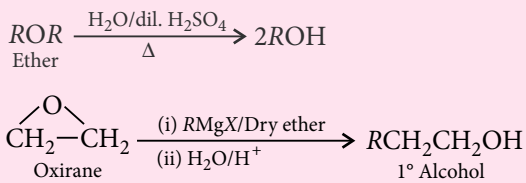
From alkenes



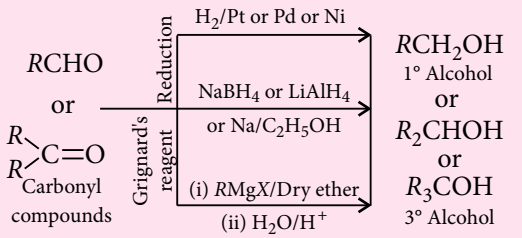
From amines



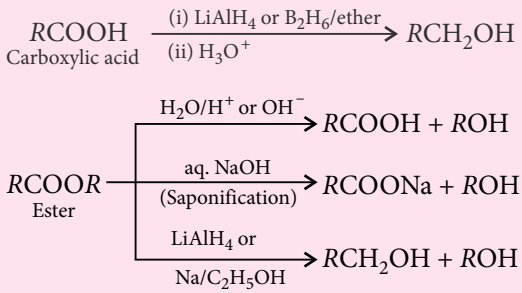
From ethers

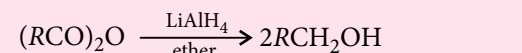


From carbonyl compounds



From acids and their derivatives





❍ **Reducing nature of different reagents**

Functional Group	Product	$LiAlH_4$/ Ether	$NaBH_4$/ EtOH	B_2H_6/ THF	H_2/ Metal
—CHO	$-CH_2OH$	✓	✓	✓	✓
>CO	>CHOH	✓	✓	✓	✓
—COOH	$-CH_2OH$	✓	×	✓	✓ (with Ru–C)
—COCl	$-CH_2OH$	✓	✓	×	✓
$(RCO)_2O$	RCH_2OH	✓	×	✓	✓
$-CO_2R$	$-CH_2OH$	✓	×	✓	✓
>C=C<	>CH—CH<	×	×	✓	✓

❑ **Physical Properties**

❍ **Physical state :** The lower members upto C_{11} are colourless mobile liquids. Higher members are wax like solids.

❍ **Odour :** The lower members have a characteristic smell (alcoholic) and a burning taste while solid members are almost colourless and tasteless.

❍ **Solubility :** The solubility in water is due to hydrogen bonding.

- The solubility in water decreases with rise of molecular mass.
- Among the isomeric alcohols, the solubility increases with increase in branching. 1° < 2° < 3°

❍ **Boiling points :** Increase gradually with increase of carbon chain as van der Waals forces increase.

- Decrease with increase of branching in carbon chain due to decrease in van der Waals forces with decrease in surface area. 1° > 2° > 3°.

KEY POINT

- The boiling points of alcohols are higher as compared to the corresponding alkanes, ethers and alkyl halides due to intermolecular hydrogen bonding.

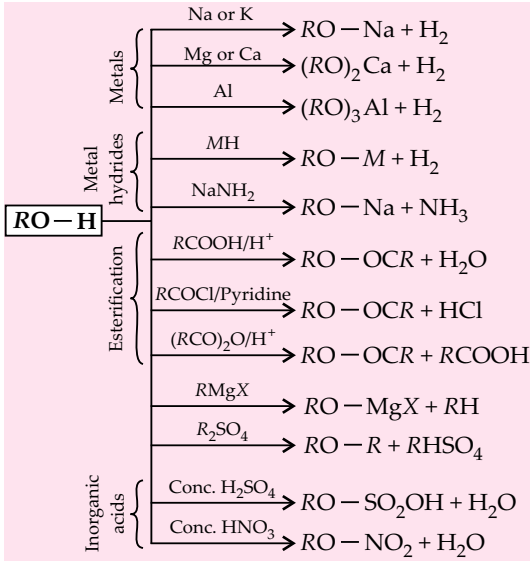
❑ **Chemical Properties**

❍ **Acidic nature :** It is due to the polar nature of O—H bond.

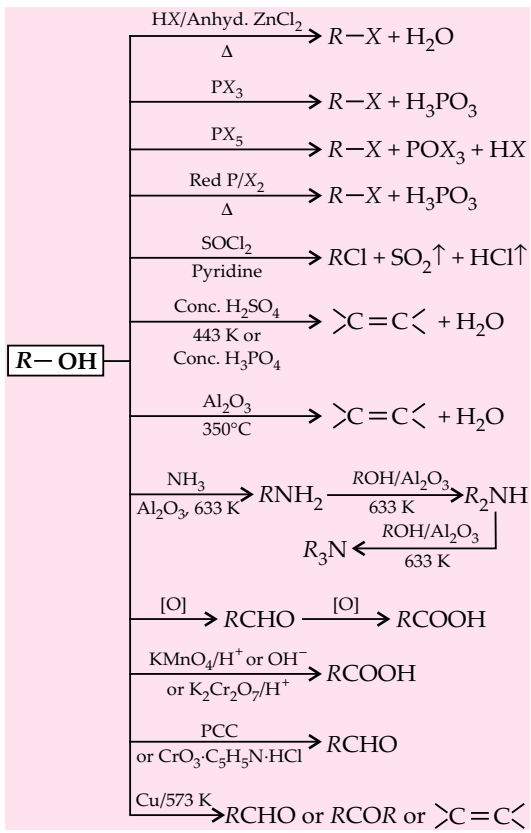
- They are weaker acids than water as water is a better proton donor than alcohol. Also, an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases.
- They act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.
- An electron releasing group increases electron density on oxygen tending to decrease the polarity of O—H bond and thus decreases the acid strength.

❑ Chemical Reactions

❍ Reactions involving cleavage of O – H bond (Alcohols act as nucleophiles.)



❍ Reactions involving cleavage of C – O bond (Alcohols act as electrophiles.)



❍ Oxidising nature of different reagents

Reagent	Purpose
Chromic acid, H_2CrO_4	1° alcohol to carboxylic acid.
Pyridinium chlorochromate (PCC)	1° alcohol to aldehyde and 2° alcohol to ketone without affecting double bond.
CrO_3/H_2SO_4	2° alcohol to ketone.
Jones reagent (chromic acid in aqueous acetone)	1° alcohol to aldehyde and 2° alcohol to ketone, without affecting double bond.
MnO_2	It selectively oxidises allylic and benzylic 1° and 2° alcohols to give aldehyde and ketones respectively.

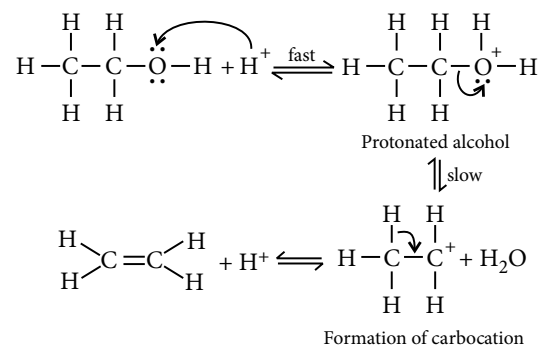
KEY POINT

- Reactivity of alcohols involving cleavage of C – OH bond is 3° > 2° > 1°.
- Reactivity of alcohols towards esterification is CH_3OH > primary > secondary > tertiary.
- Reactivity of acids towards esterification is HCOOH > CH_3COOH > CH_3CH_2COOH.

❍ Dehydration of alcohols

$$C_2H_5OH \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

❍ Mechanism



– It follows the order of stability of carbocations.
3° alcohols > 2° alcohols > 1° alcohols

- It always occurs in accordance with the Saytzeff rule *i.e.*, the more substituted alkene is the major product.
- It often gives alkenes derived from rearranged carbocations.

❑ **Distinction between 1°, 2° and 3° alcohols**

❍ **Lucas test :** An equimolar mixture of conc. HCl and anhy. $ZnCl_2$ (Lucas reagent) is added to an unknown alcohol at room temperature.
- If cloudiness appears immediately (within 5 minutes), the alcohol is 3°.
- If cloudiness appears after 5 minutes, the alcohol is 2°.
- If the solution remains clear, *i.e.*, no cloudiness is formed, the alcohol is 1°.

SELF CHECK

2. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is
(a) 1-butanol
(b) 2-butanol
(c) 2-methylpropan-2-ol
(d) 2-methylpropanol.

(AIEEE 2010)

❍ **Catalytic dehydrogenation** : It involves the passing of vapours of alcohol over reduced copper at 573 K.
- 1° alcohols give aldehydes (*dehydrogenation*).
- 2° alcohols give ketones (*dehydrogenation*).
- 3° alcohols give alkenes (*dehydration*).

❍ **Dichromate test :**
Oxidising agent : $K_2Cr_2O_7 + H_2SO_4$.
- If carboxylic acid with same number of carbon atoms as in the alcohol is formed and the colour of the solution changes from orange to green, the alcohol is 1°.
- If ketone with same number of carbon atoms as in the alcohol is formed and the colour of the solution also changes from orange to green, the alcohol is 2°.
- If the colour of the solution does not change, *i.e.*, it remains orange, the alcohol is 3°.

❍ **Victor Meyer's test :** In this test,
- Alcohol is reacted with conc. HI or red P and I_2 to form the corresponding alkyl iodide.
- Alkyl iodide is treated with silver nitrite to form corresponding nitroalkane.
- Nitroalkane is treated with nitrous acid ($NaNO_2 + H_2SO_4$) and the solution is made alkaline by addition of excess of caustic soda.
  - 1° alcohols → a blood red colour.
  - 2° alcohols → a blue colour.
  - 3° alcohols → no colour.

KEY POINT

- Benzyl and allyl alcohols react as rapidly as tertiary alcohols with Lucas reagent because their cations are resonance stabilised and stable as 3° carbocations.

❑ **Uses :** Alcohols are used

❍ as solvents for oils, fats, paints, varnishes and celluloid.

❍ for the manufacture of formaldehyde (used for the manufacture of formaldehyde resins) and formalin (used as a preservative for biological specimens).

❍ as fuel.

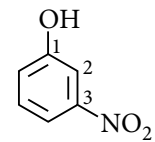
❍ as antifreeze for automobile radiators.

❍ in the preparation of dyes, medicines and perfumes.

PHENOLS

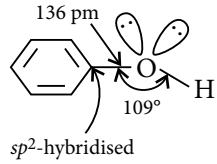
❑ Phenols are the compounds in which hydroxy (−OH) group is directly linked to aromatic ring having formula C_6H_5OH.

❑ In substituted compounds, the terms *ortho*(1,2-disubstituted), *meta*(1,3-disubstituted) and *para*(1,4-disubstituted) are used in the common names.



Common name : *m*-Nitrophenol
IUPAC name : 3-Nitrophenol

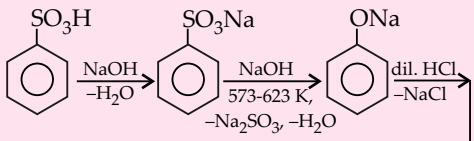
❑ Structure



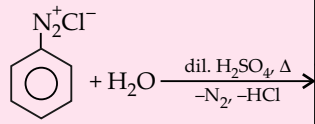
❍ C — O bond length is slightly less than that in alcohol due to partial double bond character of C — O bond and sp^2-hybridised state of C-atom to which O-atom is attached.

❑ Preparation

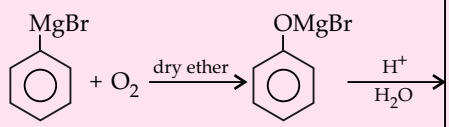
From benzenesulphonic acid



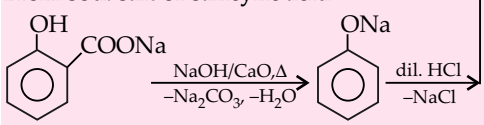
From diazonium salt

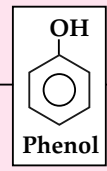


From phenylmagnesium bromide

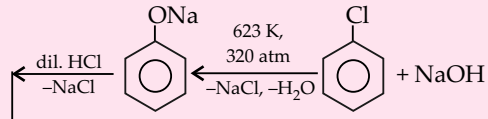


From sod. salt of salicylic acid

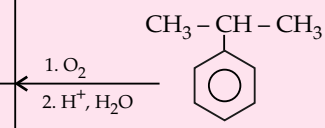




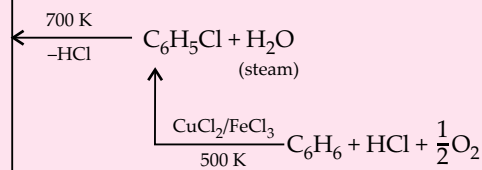
From haloarenes (Dow's process)



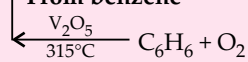
From cumene



Raschig's process



From benzene



❑ Physical Properties

❍ **Physical state :** Phenols are colourless crystalline solids or liquids.

❍ **Odour :** They have characteristic phenolic odours.

❍ **Solubility :** Like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water.

- Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.
- Phenols are soluble in alcohols, ethers and also in NaOH.

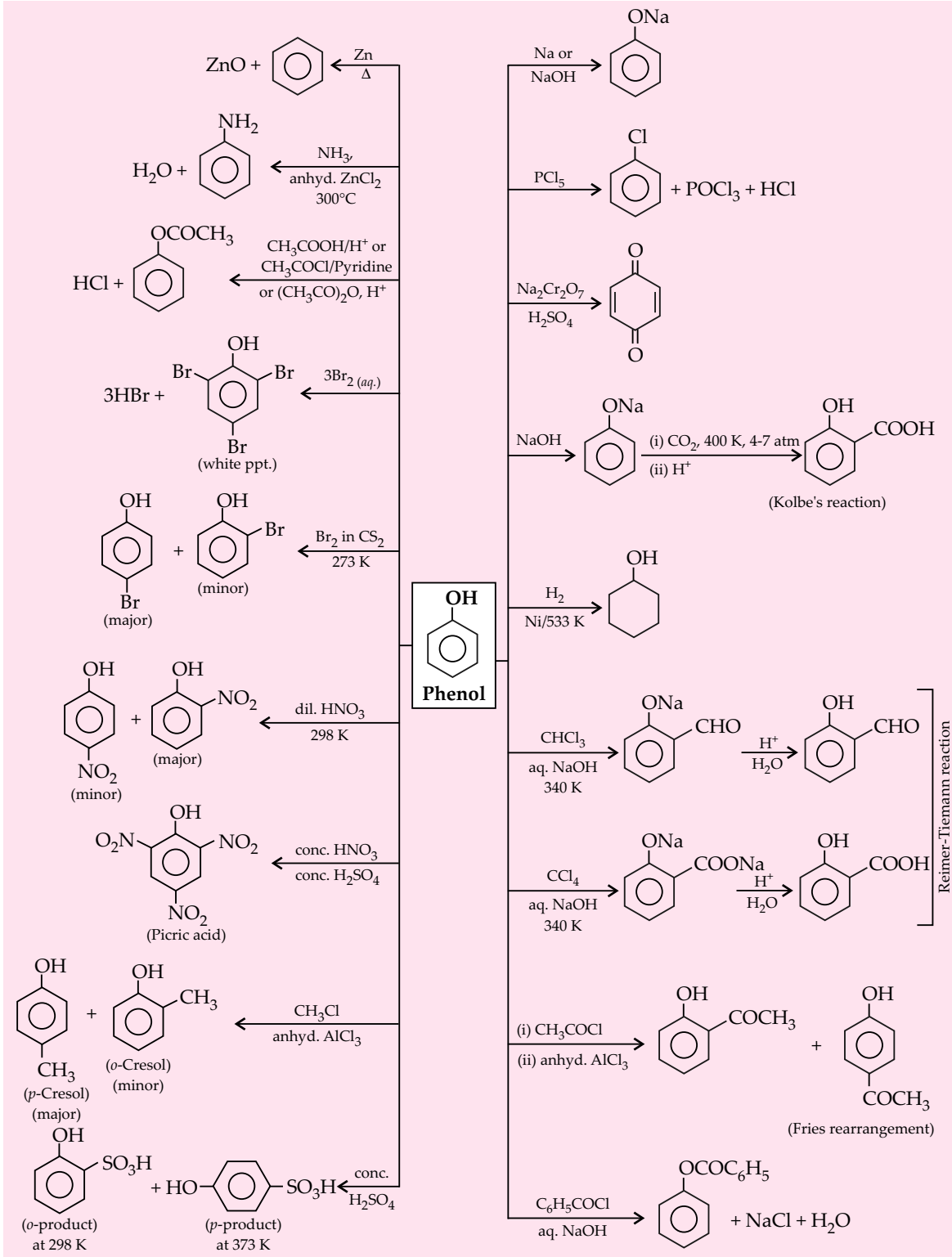
❍ **Boiling points :** Much higher than the corresponding aromatic hydrocarbons and haloarenes due to intermolecular hydrogen bonding.

❑ Chemical Properties

❍ **Acidic nature :** Phenols are weakly acidic in nature due to polar O — H bond directly attached to sp^2-hybridised C-atom.

- They turn blue litmus red and react with alkali metals and alkalies to form their salts.
- Phenol is weaker acid than carboxylic acid. It does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$).
- Phenols are more acidic than alcohols which can be explained on the basis of resonance.
- Electron withdrawing groups increase the acidic strength of phenols.
- Electron releasing groups decrease the acidic strength of phenols.

❑ Chemical Reactions



SELF CHECK

3. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is
   (a) 2-bromophenol
   (b) 3-bromophenol
   (c) 4-bromophenol
   (d) 2, 4, 6-tribromophenol.
   (AIEEE 2011)
4. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is
   (a) benzoic acid (b) salicylaldehyde
   (c) salicylic acid (d) phthalic acid.
   (AIEEE 2009)

❑ **Test for Phenols**

- **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.
- **Bromine water test :** Phenol gives white ppt. with Br_2-water due to the formation of 2, 4, 6-tribromophenol.
- **Liebermann's nitroso test :** Phenol on reaction with $NaNO_2$ and conc. H_2SO_4 gives deep green or blue colour which changes into red on dilution with water.
- **Phthalic anhydride test :** Phenol reacts with phthalic anhydride in presence of conc. H_2SO_4 and gives phenolphthalein which gives pink colour with alkali.
- **Ammonia or sodium hypochlorite test :** Phenol gives blue colour.
- **Coupling reaction :** Phenol gives orange azo dye with diazonium salt in weakly basic solution.

❑ **Uses :** Phenols are used

- in industry.
- as antiseptics in soaps, lotions and ointments.
- in the manufacture of azo dyes, phenolphthalein, etc.
- in the preparation of picric acid used as an explosive and for dyeing silk and wool.
- in the manufacture of phenol-formaldehyde plastics such as bakelite.
- in the manufacture of drugs like aspirin, salol, phenacetin, etc.

ETHERS

❑ Ethers are the compounds having general formula $C_nH_{2n+2}O$ (where $n > 1$).

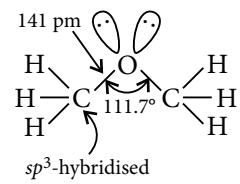
❑ Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word '*ether*' at the end.

- In IUPAC system ethers are named as alkoxyalkanes. The smaller alkyl group plus oxygen is called alkoxy substituent, while the larger alkyl group is called alkane.

  $CH_3-O-CH_2CH_2CH_3$

  Common name : Methyl *n*-propyl ether
  IUPAC name : 1-Methoxypropane

❑ **Structure**



- The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ($-R$) groups.
- The C – O bond length (141 pm) is almost the same as in alcohols.

KEY POINT

- As the size of alkyl groups in ethers increases, van der Waals repulsion increases and hence bond angle also increases.

❑ Preparation

From alcohols by dehydration

$$2ROH \xrightarrow[\text{or } Al_2O_3,\ 523\ K]{\text{conc. } H_2SO_4,\ 413\ K}$$

From alkyl halide

$$RX + RONa \xrightarrow[-NaX]{\Delta}$$

(Williamson synthesis)

$$2RX + Ag_2O(dry) \xrightarrow[-AgX]{\Delta}$$

→ ***ROR*** **Ether**

From Grignard reagent

$$ROCH_2X + R'MgX \xrightarrow[-MgX_2]{\text{Dry ether}} ROCH_2R'$$

From diazomethane

$$ROH + CH_2N_2 \xrightarrow[-N_2]{HBF_4,\Delta} ROCH_3$$

From alkenes

$$>C=C< \xrightarrow[\text{(ii) } NaBH_4,\ OH^-]{\text{(i) } Hg(OAc)_2,\ ROH} -\overset{H}{\underset{|}{C}}-\overset{OR}{\underset{|}{C}}-$$

$$>C=C< \xrightarrow[\text{or } m\text{CPBA},\ CH_2Cl_2]{RCO_3H} -\overset{O}{\underset{|}{C}}-\overset{O}{\underset{|}{C}}- + RCOOH$$

Epoxide

❑ Physical Properties

- **Physical state and odour :** Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic ethereal smell.
- **Solubility :** Ethers are soluble in water to a certain extent due to hydrogen bonding.
  - Solubility decreases with increase in molecular mass.
  - Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.
- **Boiling points :** Ethers have lower boiling points than isomeric alcohols due to their inability to form hydrogen bonds and get associated.
  - But lower ethers have slightly higher boiling points than *n*-alkanes of comparable molecular masses due to dipole-dipole interactions.
  - Higher ethers (containing carbon atom more than four) have slightly lower boiling points than *n*-alkanes of comparable molecular masses due to weak van der Waals forces of attraction.
- **Polarity :** Ethers are polar in nature.
- **Density :** Ethers have low density. All ethers are lighter than water.

❑ Chemical Reactions

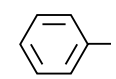
ROR →

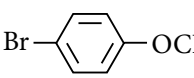
HX, 373 K	$RX + ROH$
conc. HCl	$\left[R-\overset{+}{O}(H)-R\right]Cl^-$
HI(cold)	$RI + ROH$
2HI, 373 K (Excess)	$2RI + H_2O$
PX_5, Δ	$2RX + POX_3$
H_2O/dil. H_2SO_4 under pressure, Δ	$2ROH$
conc. H_2SO_4, Δ	$ROH + ROSO_3H$
CH_3COCl, Δ Anhyd. $ZnCl_2$	$RCl + CH_3COOR$
$(CH_3CO)_2O$, Δ Anhyd. $ZnCl_2$	$2CH_3COOR$

$C_2H_5OC_2H_5$ →

Cl_2, dark	$CH_3-\underset{Cl}{\underset{\vert}{CH}}-O-\underset{Cl}{\underset{\vert}{CH}}-CH_3$
Cl_2, hυ	$C_2Cl_5OC_2Cl_5$
Al_2O_3, 360°C	$CH_2=CH_2$
CO, BF_3, 150°C, 500 atm	$C_2H_5COOC_2H_5$

SELF CHECK

5. In the reaction  $\xrightarrow{HBr}$ the products are

(a)  and H_2

(b)  and CH_3Br

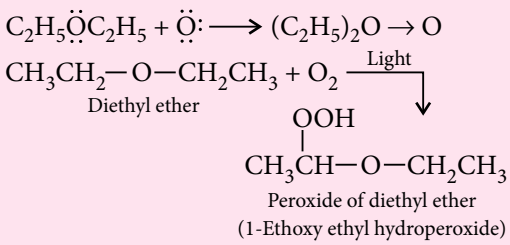
(c)  and CH_3OH

(d)  and CH_3Br

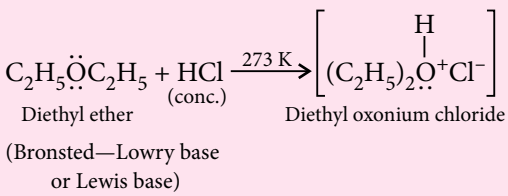
(IIT-JEE 2010)

KEY POINT

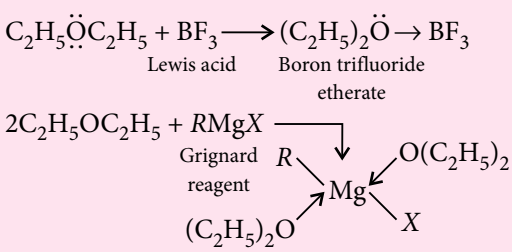
- **Reaction of ether with excess of HX :**
  - When one of the alkyl group is a 3° group, the halide formed is a 3° halide.
  - In case of anisole, the halide formed will be methyl iodide.
  - The order of reactivity with halogen acids follows : HI > HBr > HCl
- Ethers form peroxides in presence of sunlight or ultraviolet light.



- Ethers form stable oxonium salts.



- Ethers can form coordination complexes with Lewis acids like BF_3, $AlCl_3$, *R*Mg*X*, etc. known as etherates.



- ❍ **Electrophilic substitution reactions :** The alkoxy group (—O*R*) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as phenol.

❑ **Uses :** Ethers are used

- ❍ as solvents in laboratory and industry. Diethyl ether acts as a solvent for oils, fats, waxes, plastics and lacquers.
- ❍ Diethyl ether provides an inert medium for various organic reactions such as Wurtz reaction or preparation of Grignard and other organometallic reagents.

ALDEHYDES AND KETONES

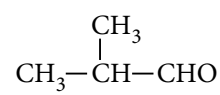
❑ These are the compounds with carbon-oxygen double bond (>C=O) called carbonyl group having general formula $C_nH_{2n}O$.

❑ Aldehydes contain carbonyl group attached to either two H-atoms or one H-atom and one C-atom of an alkyl/aryl group.

❑ In ketones, the carbonyl group is attached to two C-atoms of an alkyl/aryl group.

❑ The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.

- ❍ The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.
- ❍ The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.

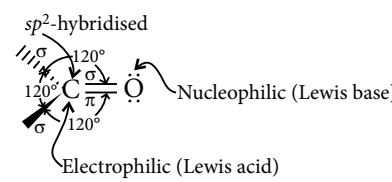


Common name : Isobutyraldehyde
IUPAC name : 2-Methylpropanal

$CH_3—CO—CH_2—CH_2—CH_3$

Common name : Methyl *n*-propyl ketone
IUPAC name : Pentan-2-one

❑ **Structure**



❑ Preparation

Aldehydes and Ketones

Oxidation of alcohols

$$RCH_2OH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + RCHO$$

$$R_2CHOH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + R-\overset{\overset{O}{\|}}{C}-R$$

Oppenauer oxidation

$$R_2CHOH + (CH_3)_2CO \xrightarrow{Al[(CH_3)_3CO]_3} (CH_3)_2CHOH + RCOR$$

Catalytic dehydrogenation of alcohols

$$RCH_2OH \xrightarrow[573\ K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\ K]{Cu} R_2CO + H_2\uparrow$$

Reductive ozonolysis of alkenes

$$RCH{=}CHR + O_3 \xrightarrow[196\ K]{CHCl_3 \text{ or } CCl_4} RCH\underset{O}{\overset{O}{<}}CHR \xrightarrow{Zn,\ H_2O} 2RCHO + ZnO$$

Rosenmund reduction

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\ S} RCHO + HCl$$

Reduction of nitriles

$$RC{\equiv}N \xrightarrow{\substack{\text{(i) } AlH(i\text{-}Bu)_2 \\ \text{(ii) } H_2O}} RCHO$$

$$RC{\equiv}N \xrightarrow{\substack{\text{(i) } R'MgX/\text{dry ether} \\ \text{(ii) } H_3O^+}} RCOR'$$

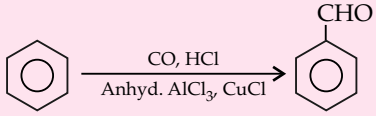
$$RC{\equiv}N \xrightarrow{\substack{\text{(i) } SnCl_2 + HCl \\ \text{(ii) Ether} \\ \text{(iii) } H_2O}} RCHO + NH_4Cl$$

(Stephen reduction)

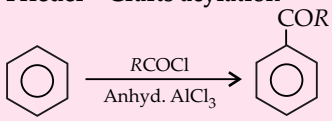
From esters

$$RCOOR \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H, 195 K}} RCHO$$

Gatterman—Koch reaction



Friedel—Crafts acylation



From alkynes

$$-C{\equiv}C- \xrightarrow[HgSO_4,\ 333\ K]{dil.\ H_2SO_4} RCHO \text{ or } RCOR$$

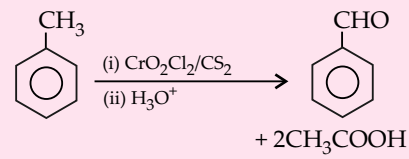
$$-C{\equiv}C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\ THF} RCHO \text{ or } RCOR$$

Oxidation of 1,2-glycols

$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO + 2CH_3COOH + (CH_3COO)_2Pb$$

$$R-\underset{R}{\overset{OH}{C}}-\overset{OH}{C}-\underset{R'}{R'} \xrightarrow{[O]} RCOR + R'COR'$$

Etard reaction



Oxo process

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[100°C,\ \text{pressure}]{[Co(CO)_4]_2} RCH_2CH_2CHO$$

Wacker process

$$H_2C{=}CH_2 + PdCl_2 + H_2O \xrightarrow[\text{Air or } O_2]{CuCl_2} CH_3CHO + Pd + 2HCl$$

From alkyl halides

$$RCH_2X + (CH_3)_2SO \longrightarrow RCHO + (CH_3)_2S + HX$$

$$R_2CHX + (CH_3)_2SO \longrightarrow R_2CO + (CH_3)_2S + HX$$

From lithium and cadmium salts

$$2RMgX + CdCl_2 \xrightarrow[\text{ether}]{dry} R_2Cd + 2Mg(X)Cl$$

$$R_2Cd + R'COCl \longrightarrow RCOR' + RCdCl$$

$$R-COO^-\,Li^+ + CH_3Li \longrightarrow R-\underset{OLi}{\overset{OH}{C}}-CH_3 \xrightarrow{H^+/H_2O} R-\underset{OH}{\overset{OH}{C}}-CH_3 \xrightarrow{-H_2O} R-\overset{\overset{O}{\|}}{C}-CH_3$$

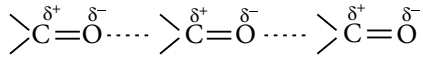
SELF CHECK

6. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of
   (a) two ethylenic double bonds
   (b) a vinyl group
   (c) an isopropyl group
   (d) an acetylenic triple bond.

(AIEEE 2011)

❑ Physical Properties

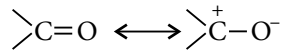
- **Physical state and odour :** Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
  - However, solubility decreases with increase in molecular weight.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - However all carbonyl compounds are fairly soluble in organic solvents.
- **Boiling points :** Slightly lower than corresponding alcohol due to lack of hydrogen bonding.
  - Their boiling points are slightly higher than those of corresponding non-polar hydrocarbons or weakly polar ethers. This is due to intermolecular dipole-dipole interaction among polar aldehydes or ketones.



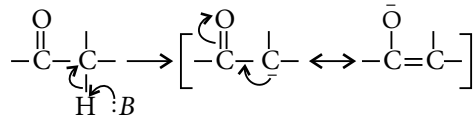
  - Among isomeric aldehydes and ketones, boiling points of ketones are slightly higher than those of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

❑ Chemical Properties

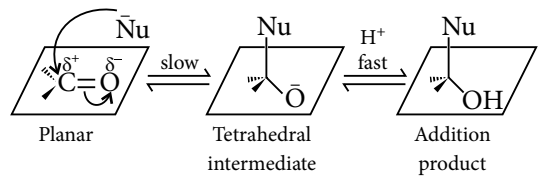
- **Polarity of carbonyl ($>C=O$) group :** Aldehydes and ketones undergo nucleophilic addition reactions in contrast to alkenes which undergo electrophilic addition reactions.



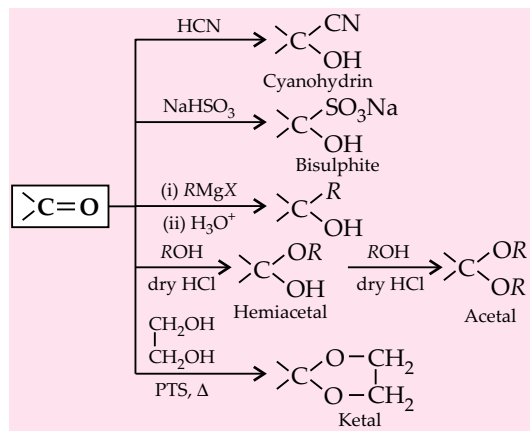
- **Acidity of α-hydrogen atoms :** The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



- **Nucleophilic addition reactions :**

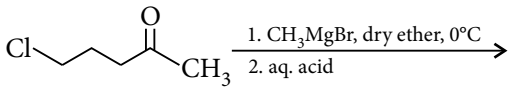


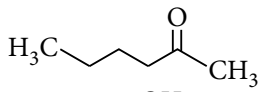
  - *Reactivity order* :
    Aldehydes > Ketones
    (steric and electronic reasons)
    HCHO > *R*CHO > PhCHO > *R*CO*R*
    > *R*COPh > PhCOPh

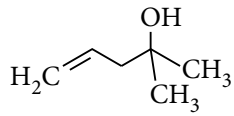


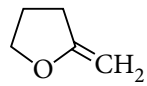
SELF CHECK

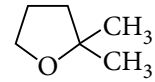
7. The major product in the following reaction is



(a) 

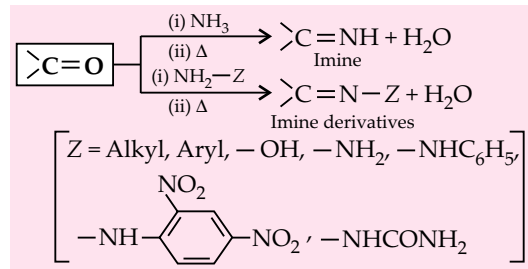
(b) 

(c) 

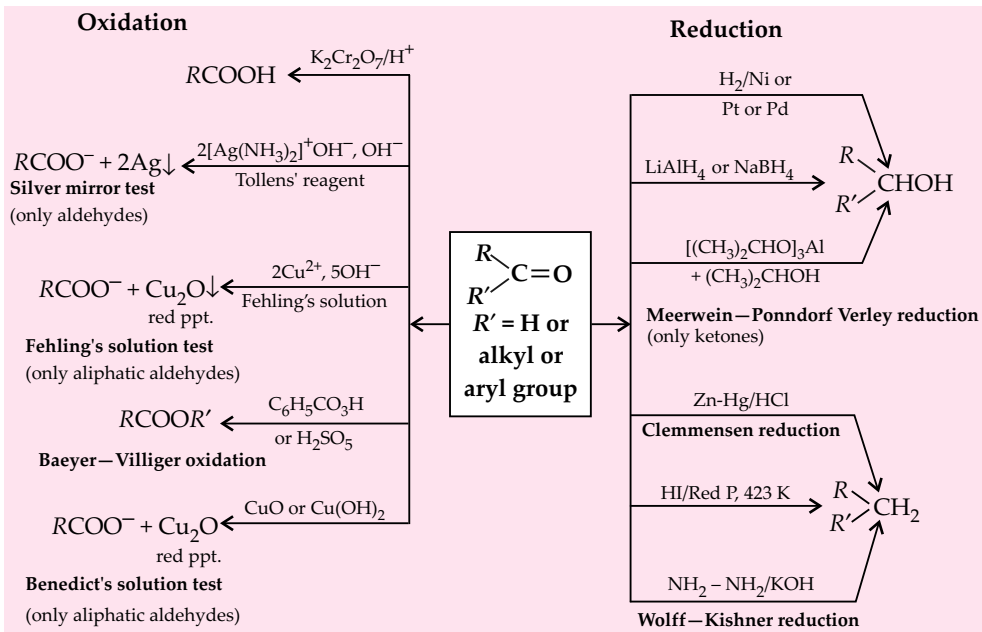
(d) 

(JEE Advanced 2014)

❍ Nucleophilic addition - elimination reactions :



❍ Oxidation and reduction reactions :



❍ Haloform reaction :

Given by methyl ketones (even acetaldehyde).

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$RCOCH_3 + 3NaOI \longrightarrow RCOONa + CHI_3\downarrow + 2NaOH$

Iodoform (yellow ppt.)

KEY POINT

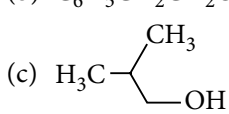
- Haloform test is also given by alcohols containing CH_3CHOH- group linked to C or H-atom *e.g.*, ethanol, propan-2-ol, butan-2-ol.

SELF CHECK

8. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is

(a) $CH_3CH_2CH(OH)CH_2CH_3$

(b) $C_6H_5CH_2CH_2OH$

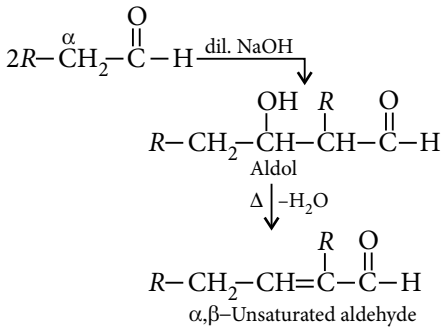
(c) 

(d) $PhCHOHCH_3$

(AIEEE 2006)

❍ **Reactions involving α-hydrogen atom :**

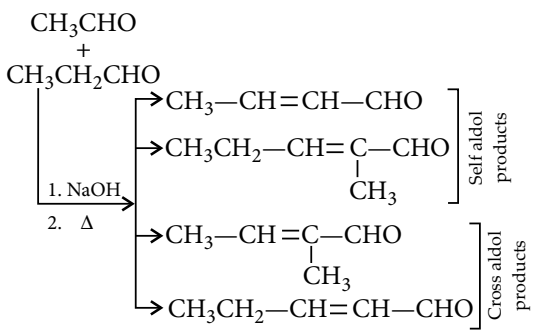
– *Aldol condensation* :



– *Intramolecular aldol condensation* : It takes place in diketones and gives rise to cyclic products.

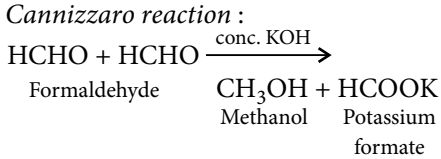
– *Crossed aldol condensation* : Aldol condensation is carried out between two different aldehydes and/or ketones.

– If both of them contain α-hydrogen atoms, it gives a mixture of four products.

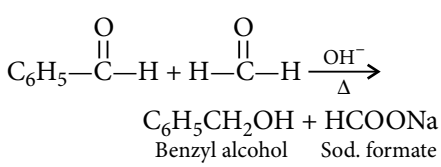


❍ **Reactions involving no α-hydrogen atom :**

– *Cannizzaro reaction* :



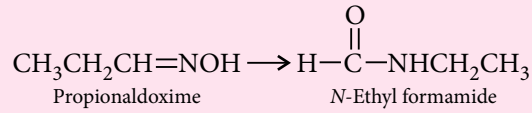
– *Crossed Cannizzaro reaction* :



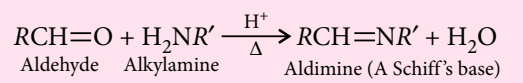
– *Intramolecular Cannizzaro reaction* : It is given by dialdehydes having no α-hydrogen atoms.

KEY POINT

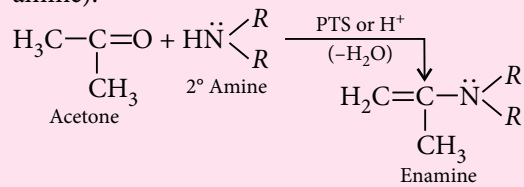
- Ketoximes on treatment with acid catalyst such as conc. H_2SO_4, PCl_5, H_3PO_4, $SOCl_2$ or $C_6H_5SO_2Cl$, etc., undergo **Beckmann rearrangement** to form a substituted amide.
- This rearrangement is intramolecular and involves 1,2-shift. It is always the anti $-R$ group that migrates in the Beckmann rearrangement.



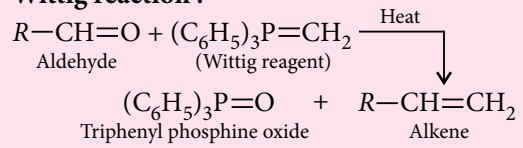
- The nucleophilic addition-elimination reactions with ammonia derivatives (NH_2-Z) are carried out in weakly acidic medium (pH = 3–4).
- Aldehydes and ketones react with primary amines to form azomethines (imines) known as **Schiff's base**.



- Aldehydes and ketones that have at least one α-hydrogen reacts with secondary amines to form enamines (α, β-unsaturated tertiary amine).

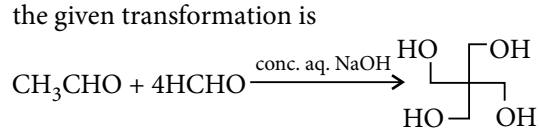


- **Wittig reaction :**



SELF CHECK

9. The number of aldol reaction(s) that occurs in the given transformation is



(a) 1 (b) 2
(c) 3 (d) 4

(IIT- JEE 2012)

10. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is
(a) 2,2,2-trichloroethanol
(b) trichloromethanol
(c) 2,2,2-trichloropropanol
(d) chloroform.

(AIEEE 2011)

- **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

- **Distinction between aldehydes and ketones**

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Black precipitate of silver or silver mirror	No black ppt. or silver mirror
2,4-Dinitro-phenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones
Sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test)	No reaction
Alkaline sodium nitroprusside	A deep red colour (formaldehyde does not respond to this test)	Red colour which changes to orange

Uses

- **Formaldehyde :** It is used in the
  - preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.
  - manufacture of synthetic dyes such as *para*-rosaniline, indigo, etc.
- **Acetaldehyde :** It is used
  - as an antiseptic inhalant in nose troubles.
  - in the preparation of paraldehyde (hypnotic) and metaldehyde (solid fuel).
- **Acetone :** It is used
  - as a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.
  - in the preparation of chloroform, iodoform, sulphonal and chloretone.

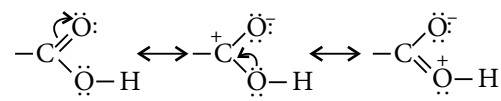
CARBOXYLIC ACIDS

- Compounds having –COOH group having general formula $C_nH_{2n}O_2$.
- The common names end with the suffix –'*ic acid*' and have been derived from Latin or Greek names of their natural sources.
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –'*e*' in the name of the corresponding alkane with –'*oic acid*'.

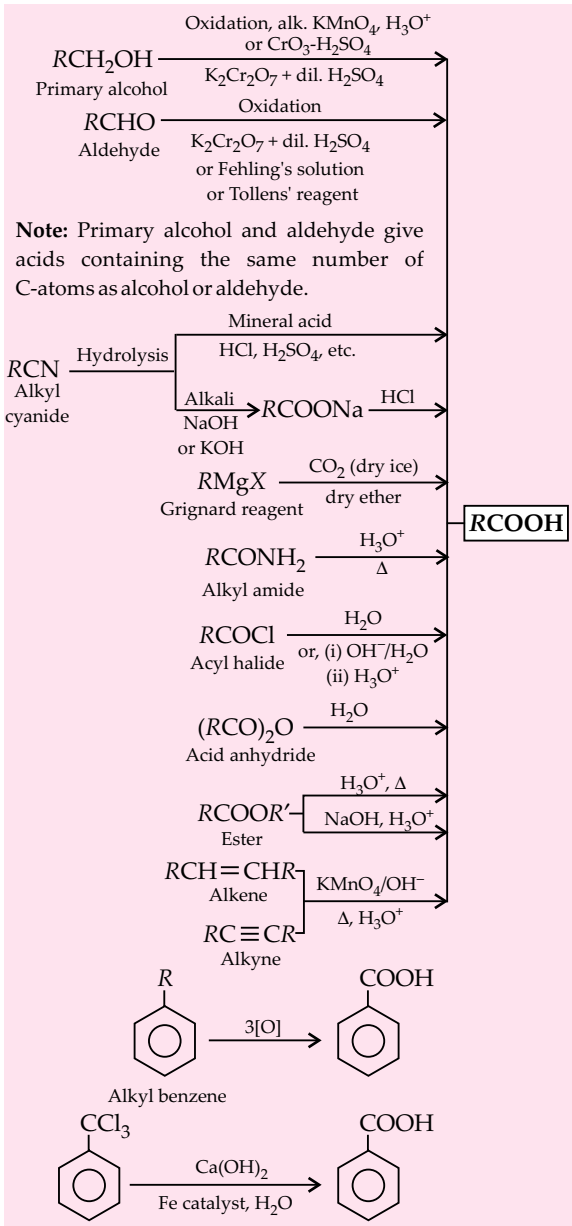
    $CH_3CH_2CH_2COOH$

    Common name : Butyric acid

    IUPAC name : Butanoic acid
- **Structure :** The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



❑ Preparation

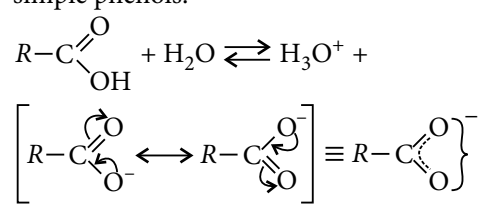


❑ Physical Properties

- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
  - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
  - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
  - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.
- **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

❑ Chemical Properties

- **Acidic nature :** Carboxylic acids are weaker acids than mineral acids, but they are stronger acids than alcohols and many simple phenols.



- **Effect of substituents on acidic strength :**
  - Presence of electron withdrawing groups, increases the acidic strength.
  - More the number of electron withdrawing groups, more will be the acidic strength.
  - More is the distance between the carboxyl group and electron withdrawing group, less will be the acidic strength.
  - Presence of electron releasing groups, decreases the acidic strength.

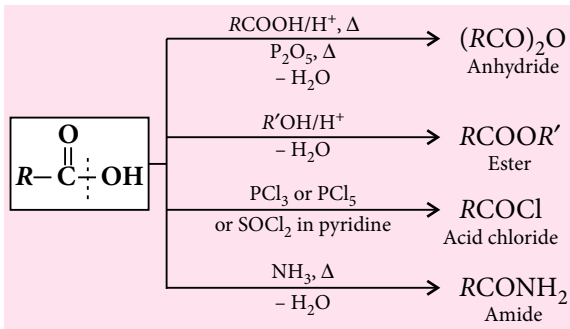
SELF CHECK

11. Among the following compounds, the most acidic is
    (a) *p*-nitrophenol
    (b) *p*-hydroxybenzoic acid
    (c) *o*-hydroxybenzoic acid
    (d) *p*-toluic acid.

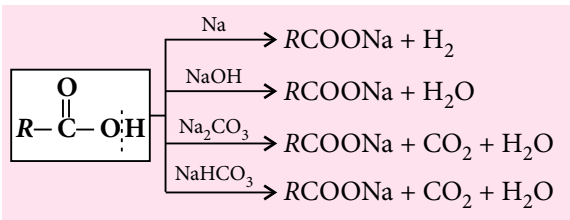
(IIT-JEE 2011)

❑ Chemical Reactions

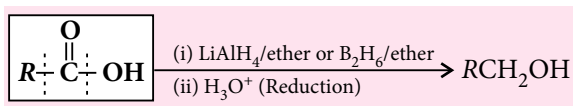
❍ Reactions involving —OH group :



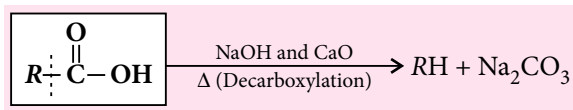
❍ Reactions involving proton of —OH group :



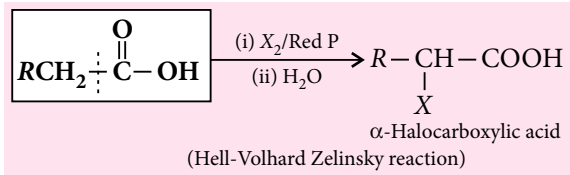
❍ Reaction involving $>C=O$ group :



❍ Reaction involving —COOH group :

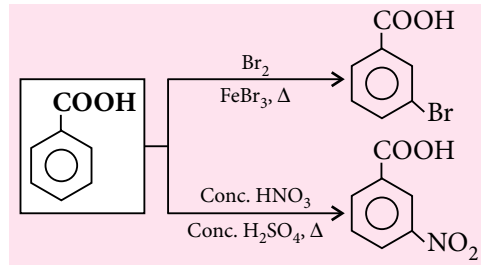


❍ Reaction involving —*R* group :



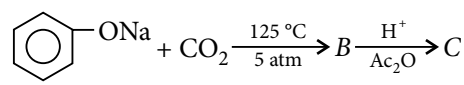
❍ Ring substitution in aromatic acids :

—COOH group is deactivating and *meta* directing.

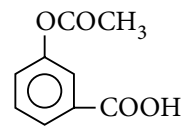


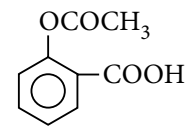
SELF CHECK

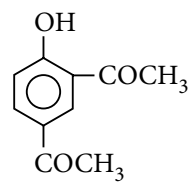
12. Sodium phenoxide when heated with CO_2 under pressure at 125 °C yields a product which on acetylation produces *C*.

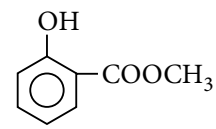


The major product *C* would be

(a) 

(b) 

(c) 

(d) 

(JEE Main 2014)

13. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was
    (a) CH_3OH (b) HCHO
    (c) CH_3COCH_3 (d) CH_3COOH

(AIEEE 2009)

❑ Distinction Test between Phenol and Carboxylic Acid

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas
$FeCl_3$ test	Violet colour	Buff coloured ppt.

Uses

- **Formic Acid :** It is used
  - as a coagulating agent for latex in rubber industry.
  - for dehydration of halides in leather industry.
- **Acetic Acid :** It is used
  - as vinegar and for manufacturing pickles.
  - for making various dyestuffs, perfumes and medicines.

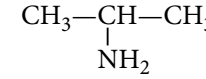
ORGANIC COMPOUNDS CONTAINING NITROGEN

- Preparations, Properties, Reactions and Uses
- Amines, Aniline and Diazonium Salts

TIPS TO REMEMBER

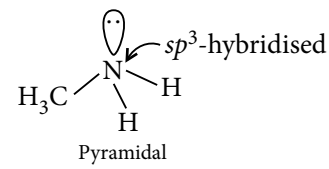
AMINES

- The derivatives of ammonia formed by the replacement of one or more hydrogen atoms by the corresponding number of alkyl or aryl groups are known as amines.
- In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, alkylamine as one word.
  - In IUPAC system, amines are named as *alkanamines*, derived by replacement of '*e*' of alkane by the word '*amine*'.



Common name : Isopropylamine
IUPAC name : Propan-2-amine

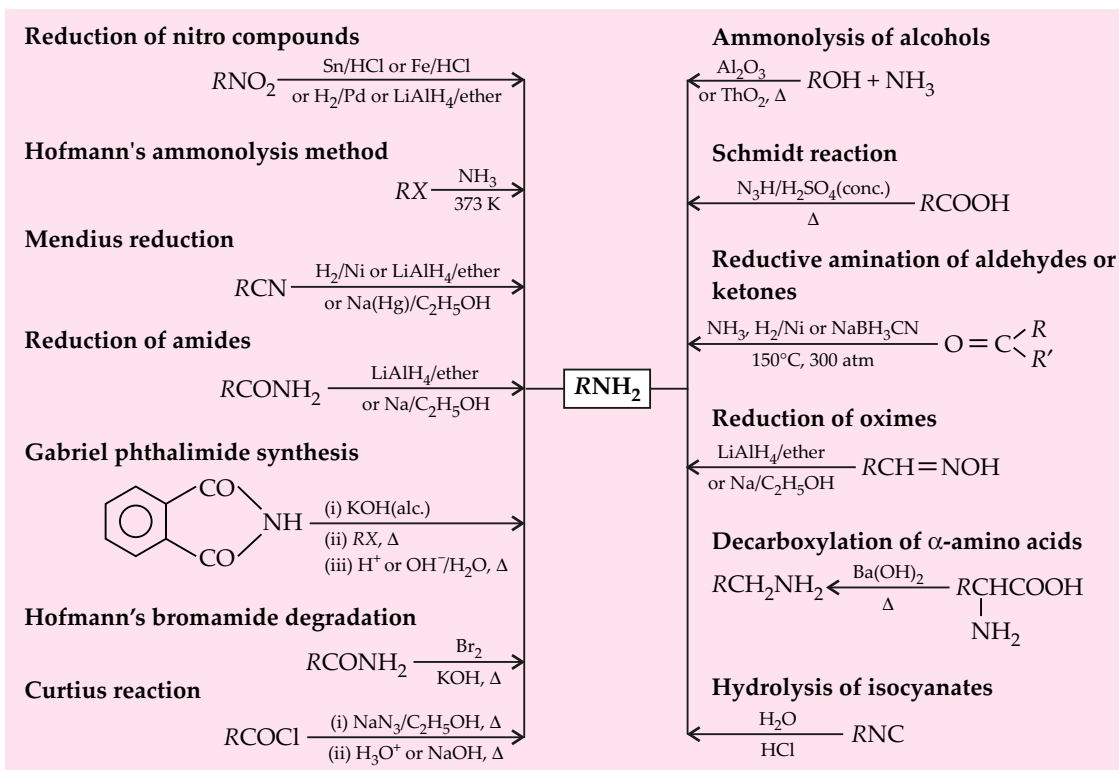
- **Structure**



Pyramidal

  - The angle C — N — *R*, (where *R* is C or H) is less than 109.5° due to the presence of lone pair on N-atom.

- **Preparation**



KEY POINT

- The amines of the type $R_1R_2R_3N$ exist in the form of racemic mixture that cannot be resolved into enantiomers because of rapid inversion of an enantiomer to its mirror image. This inversion is called **amine inversion, nitrogen inversion** or **flipping**. During this, the state of hybridisation of N changes from sp^3 to sp^2.

SELF CHECK

14. An organic compound *A* upon reacting with NH_3 gives *B*. On heating, *B* gives *C*. *C* in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is
    (a) CH_3CH_2COOH
    (b) CH_3COOH
    (c) $CH_3CH_2CH_2COOH$
    (d) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—COOH$

(JEE Main 2013)

❑ **Physical Properties**

❍ **Physical state and odour :** Lower aliphatic amines are gases with smell like ammonia.
- Lower aromatic amines are liquids with characteristic unpleasant odour but higher ones are solids which are odourless.

❍ **Solubility :** Amines are soluble in water as they can form hydrogen bonds with water.
- As the size of alkyl group increases, solubility decreases.
- Higher amines are insoluble in water but soluble in organic solvents.
- Aromatic amines are insoluble in water. They are soluble in organic solvents such as benzene, ether, alcohol.

❍ **Boiling points :** Amines show higher boiling points than hydrocarbons of comparable molecular masses due to intermolecular hydrogen bonds.
- Tertiary amines have the lowest boiling points as they do not have hydrogen atoms linked to the nitrogen atom.
- The intermolecular association is more in primary amines than in secondary amines due to presence of two hydrogen atoms. Therefore, the order of boiling points of isomeric amines is 1° > 2° > 3°.

❑ **Chemical Properties**

❍ **Basic nature :** Due to the presence of lone pair of electrons on nitrogen atom, amines are basic in nature.
- Basic character of amines can be compared on the basis of inductive effect of alkyl groups, steric effect and resonance involvement of lone pair of electrons.
- Among aliphatic amines *+I* effect of alkyl groups pushes the electrons towards nitrogen atom and so increases the basic character.
- In gas phase, the order of basic character is : 3 ° > 2° > 1° > NH_3
- In aqueous solution, the order of basic character is : 2 ° > 1° > 3° > NH_3 (for methylamines) and 2° > 3° > 1° > NH_3 (if alkyl group is bigger than methyl group).
  This is due to the reason that when alkyl group is small, there is no steric hindrance to H-bonding hence stability due to H-bonding predominates. However when alkyl group is bigger, there will be some steric hindrance to H-bonding and stability due to *+I* effect predominates.

SELF CHECK

15. Amongst the following the most basic compound is
    (a) benzylamine (b) aniline
    (c) acetanilide (d) *p*-nitroaniline

(AIEEE 2005)

KEY POINT

- Aliphatic amines are stronger bases than ammonia due to the *+I* effect of alkyl groups present in amines.
- Aromatic amines are weaker bases than ammonia due to *–I* effect of aryl group.

CONCEPT MAP

THERMODYNAMICS

Branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

Thermodynamic Terms

System

Specified part of the universe which is under investigation.

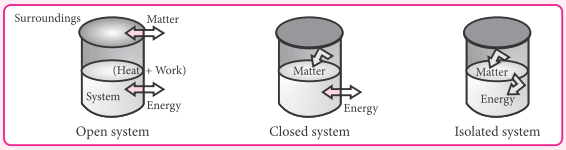
Surroundings

Remaining part of the universe which can interact with the system.

Open system : Can exchange both matter and energy.

Closed system : Can exchange energy but not matter.

Isolated system : Neither matter nor energy can be exchanged.



Thermodynamic Properties

Physical quantities used to define the state of a system.

Intensive Properties : Do not depend upon the quantity or size of matter present in the system. *e.g.*, pressure, temperature, density, surface tension, viscosity, specific heat, melting and boiling points, etc.

Extensive Properties : Depend upon the quantity or size of matter present in the system. *e.g.*, mass, volume, internal energy, entropy, enthalpy, etc.

- Extensive properties are additive but intensive properties are not.

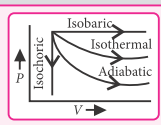
Thermodynamic Processes

Isothermal Process : At constant temperature, $dT = 0$

Isobaric Process : At constant pressure, $dP = 0$

Isochoric Process : At constant volume, $dV = 0$

Adiabatic Process : Completely insulated, $dq = 0$



State Functions

Properties which depend only on the initial and final states of a system *i.e.*, do not depend on the path followed. *e.g.*, pressure, volume, temperature, entropy, enthalpy, internal energy, etc.

Path Functions

Properties which depend upon the path followed. *e.g.*, work, heat.

Work : Mode of energy exchanged between the system and the surroundings as a result of pressure difference between them.

- $w_{\text{irreversible}} = p_{ext}(V_f - V_i)$
- $w_{\text{reversible}} = -2.303\, nRT \log \frac{V_f}{V_i}$ or $-2.303\, nRT \log \frac{P_i}{P_f}$
- Work done by the system is –ve.
- Work done on the system is +ve.

Heat : Mode of energy exchanged between the system and the surroundings as a result of temperature difference between them.

- Heat given out by the system is –ve.
- Heat absorbed by the system is +ve.
- $q = C\Delta T$; $C_p - C_v = nR$; $\gamma = C_p/C_v$

Have a Look!

- For isothermal expansion of an ideal gas against vacuum (free expansion), $\Delta U = 0$ as $w = 0$ and $q = 0$.
- For all isothermal processes involving ideal gas, $\Delta U = 0$.
- During adiabatic expansion of a real gas and isothermal expansion of an ideal gas, enthalpy remains constant.
- For elementary substances in the standard state, the standard enthalpy of formation ($\Delta_f H°$) is taken as zero.
- When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence, arranged in a more ordered manner *i.e.*, randomness decreases.
- When an egg is boiled, entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

Laws of Thermodynamics

First Law of Thermodynamics

- $\Delta U = q + w$
- For adiabatic change, $\Delta U = w_{ad}$ as $q = 0$.
- For isochoric change, $\Delta U = q_v = C_v \Delta T$ as $\Delta V = 0$.

Internal Energy Change (ΔU)

Heat absorbed or evolved by the system at constant volume.

- $\Delta U = U_P - U_R$

Enthalpy Change (ΔH)

Heat absorbed or evolved by the system at constant pressure.

- $\Delta H = q_p = C_p \Delta T$, $\Delta H = \Delta U + P\Delta V$ or $\Delta U + \Delta n_g RT$

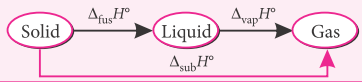
Reaction Enthalpy: Enthalpy change accompanying a reaction.

- $\Delta_r H = \sum H_P - \sum H_R$

Standard Enthalpy of Reaction ($\Delta_r H°$): Enthalpy change of a reaction when all the participating substances are in their standard states.

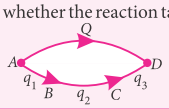
Standard Enthalpy of Formation ($\Delta_f H°$): Enthalpy change accompanying the formation of one mole of a substance from its constituents in their standard states.

Enthalpy Change during Phase Transformation: Enthalpy change accompanying the conversion of 1 mole of a substance from one state to another.



Hess's Law of Constant Heat Summation

Heat change accompanying a reaction is always same whether the reaction takes place in one step or in multisteps.



$Q = q_1 + q_2 + q_3$

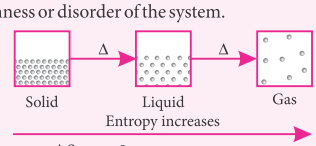
Second Law of Thermodynamics

For a spontaneous process, the entropy of the universe is continuously increasing.

Entropy (S)

Measure of randomness or disorder of the system.

- $\Delta S = \frac{\Delta H}{T}$



- For reversible process, $\Delta S_{\text{total}} = 0$
- For irreversible process, $\Delta S_{\text{total}} > 0$

Gibbs Free Energy (G)

Net energy available to do useful work.

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G° = -nFE°_{\text{cell}}$
- $\Delta G° = -2.303RT \log K$

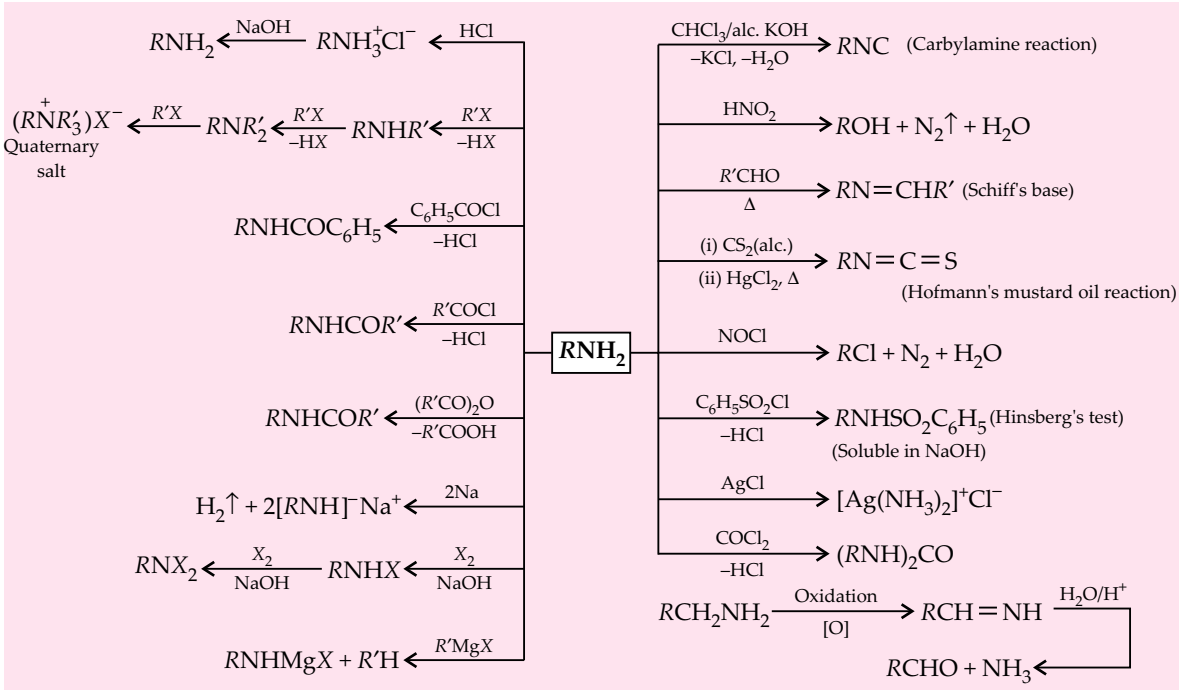
Criteria for spontaneity

- If $\Delta G < 0$ - process is spontaneous.
- If $\Delta G = 0$ - process is at equilibrium.
- If $\Delta G > 0$ - process is non-spontaneous.

Third Law of Thermodynamics

The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero.

❑ Chemical Reactions



SELF CHECK

16. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is

(a) 6 (b) 2

(c) 5 (d) 4

(JEE Main 2013)

❑ Distinction between 1°, 2° and 3° amines

- **Hinsberg's test :** It involves the treatment of the mixture with benzene sulphonyl chloride ($C_6H_5SO_2Cl$) called Hinsberg's reagent. The solution is then made alkaline with aqueous alkali.
  - Primary amine forms *N*-alkylbenzene sulphonamide which is soluble in alkali.
  - Secondary amine forms *N*, *N*-dialkyl benzene sulphonamide which is insoluble in alkali.
  - Tertiary amine does not react.
- **Hofmann test :** It involves the treatment of the mixture with diethyl oxalate (Hofmann's reagent).
  - Primary amine forms a solid dialkyl oxamide.
  - Secondary amine forms a liquid dialkyl oxamic ester.
  - Tertiary amine does not react.
- **Carbylamine test :** It involves the heating of the mixture with chloroform in presence of alcoholic potassium hydroxide to form isocyanides (or carbylamines) which possess foul smell.
  - Only aliphatic and aromatic primary amines give this test.
- **Azo dye test :** It involves the treatment of aniline with nitrous acid at 0-5°C and alkaline solution of β-naphthol.
  - Only primary aromatic amines will give orange coloured azo dyes.
- **Hofmann mustard oil reaction :** Both aromatic and aliphatic primary amines give this test.

- Aliphatic primary amines on heating with CS_2 and $HgCl_2$ give characteristic smell like mustard oil.
- Aromatic primary amines on heating with ethanolic CS_2 and solid KOH give *N*,*N*′-diphenylthiourea which on treatment with conc. HCl gives phenyl isothiocyanate.

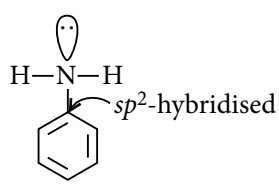
❍ **Nitrous acid test :** Aromatic primary amines react with nitrous acid at 0-5°C and give benzenediazonium salts.
- Aliphatic primary amines react with cold nitrous acid at 0-5°C and give alcohols with the evolution of nitrogen gas.
- Both secondary aliphatic and aromatic amines with nitrous acid give yellow oily compounds called *N*-nitrosamines.
- Tertiary aliphatic amines with nitrous acid give water soluble nitrite salts while aromatic tertiary amines udergo electrophilic substitution to form green coloured *p*-nitroso-*N*, *N*-dialkylamine.

❑ **Uses :** Lower aliphatic amines are used
❍ as solvents in laboratory and industry.
❍ in petroleum refining.
❍ in the manufacture of detergents.

ANILINE

❑ It is an aromatic amino compound in which the nitrogen atom of amino group is directly attached to aromatic ring.

❑ **Structure**



❑ **Physical Properties**
❍ Fresh aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.
❍ Its boiling point is 183°C.
- High boiling point of aniline is due to intermolecular H-bonding.
- *p*-Substituted anilines, being the most symmetric, have the highest melting points.

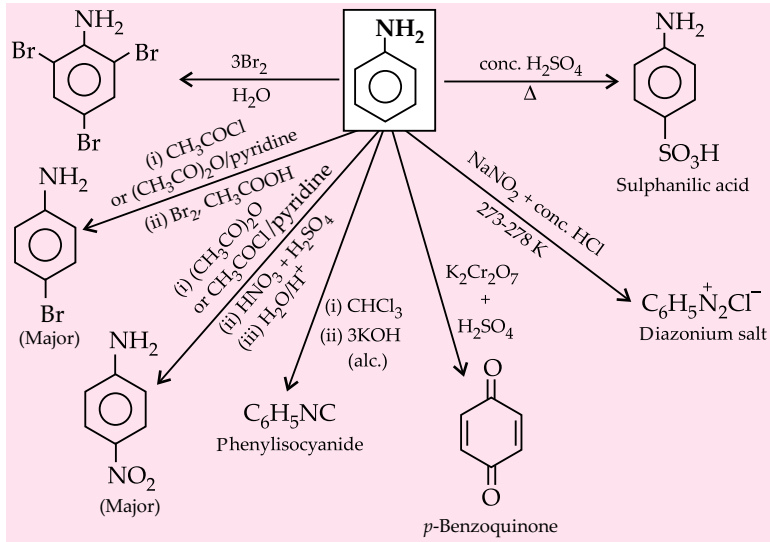
❍ It is slightly heavier than water.
❍ It has a characteristic odour which is not pleasant.
❍ It is slightly soluble in water but readily soluble in organic solvents.
❍ It is steam volatile.
❍ It is toxic in nature.

❑ **Chemical Properties**
❍ **Basic nature :** Aromatic amines like aniline are less basic than aliphatic amines because of the involvement of lone pair of electrons in resonance with the aromatic ring which now becomes less available for donation.
- Also sp^2-hybridised carbon of the aromatic ring is more electron withdrawing than sp^3-hybridised carbon of aliphatic amines and exerts a stronger withdrawing effect resulting in less tendency to donate lone pair.
- In substituted aromatic amines, electron withdrawing groups decrease the basic character and electron releasing group increase the basic character.

KEY POINT

- Due to a combination of steric and electronic factors, *o*-substituted anilines are weaker bases than anilines regardless of the nature of the substituent whether electron donating or electron withdrawing. This is called **ortho-effect**.

❑ **Chemical Reactions**
❍ Aniline undergoes electrophilic substitution reactions. $-NH_2$ group is *ortho* and *para* directing group.



- **Uses :** Aromatic amines are used
  - in the manufacture of dyes and drugs.
  - as antioxidants.

DIAZONIUM SALTS

- **General Formula :** $ArN_2^+X^-$, where Ar stands for the aryl ($-C_6H_5$) group and X^- is Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-.
- **Preparation**

$$\underset{\text{Aniline}}{C_6H_5NH_2} + NaNO_2 + 2HCl \xrightarrow{0\text{-}5^\circ C} \underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+Cl^-} + NaCl + 2H_2O$$

Mechanism :

First step :

$$HO-N=O + HCl \longrightarrow H_2O^+-N=O \xrightleftharpoons{-H_2O} \underset{\text{Nitrosonium ion}}{N\equiv O}$$

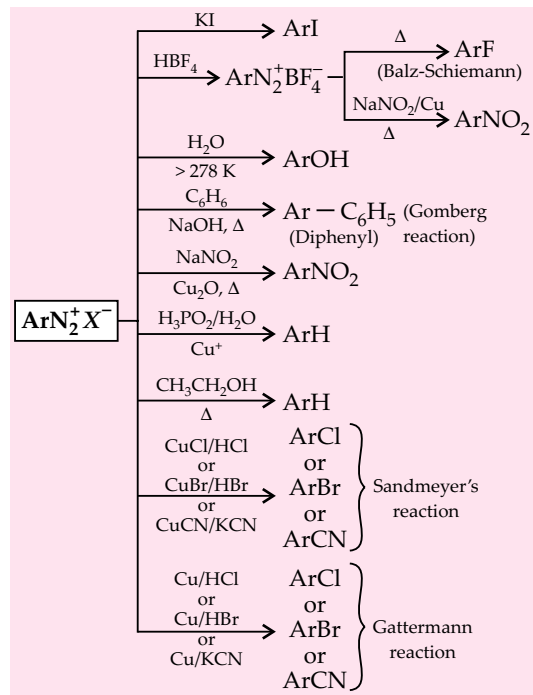
Second step :

$$C_6H_5-\ddot{N}H_2 + N=O \longrightarrow C_6H_5-\overset{H}{\overset{|}{\overset{+}{N}}}-N=O$$

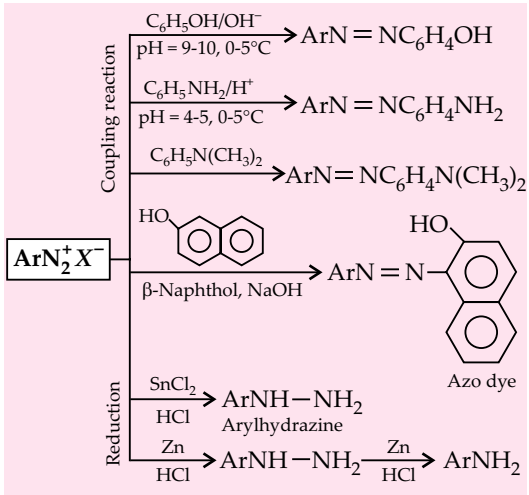
$$C_6H_5-N=N-\overset{+}{O}H_2 \xrightleftharpoons[-H^+]{+H^+} C_6H_5-N=N-OH$$

$$C_6H_5-N=N-OH \xrightarrow{-H_2O} C_6H_5-N\equiv N$$

- **Stability :** Arenediazonium salts are more stable (for short time) than alkanediazonium salts due to dispersal of positive charge over the benzene ring.
- **Physical Properties**
  - These are generally colourless, crystalline solids, which are soluble in water.
  - They are unstable and explode in dry state.
- **Chemical Properties**
  - **Reactions involving displacement of diazo group :**



❍ **Reactions involving retention of diazo group :**



❑ **Uses**

❍ Diazonium salts have many synthetic applications for preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene.

❍ They are also used for the preparation of azo dyes and indicators like methyl orange.

ANSWER KEYS (SELF CHECK)

1. (c)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (d)
6. (b)	**7.** (d)	**8.** (d)	**9.** (c)	**10.** (a)
11. (c)	**12.** (b)	**13.** (d)	**14.** (a)	**15.** (a)
16. (c)				

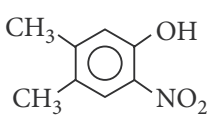
Exam Café

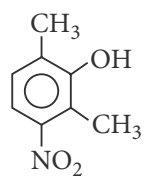
QUESTIONS FOR PRACTICE

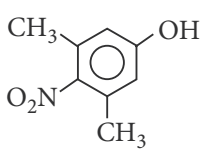
1. The major product formed in reaction of 3-methylbutan-2-ol with conc. HCl is
(a) 2-chloro-2-methylbutane
(b) 2-chloro-3-methylbutane
(c) 2-methylbut-2-ene
(d) 2-methylbut-1-ene.

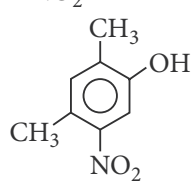
2. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI, it gives only one type of alkyl halide. The compound is
(a) ethoxyethane (b) 2-methoxypropane
(c) 1-methoxypropane (d) 1-butanol.

3. Which one of the following phenols is the strongest acid?

(a) 

(b) 

(c) 

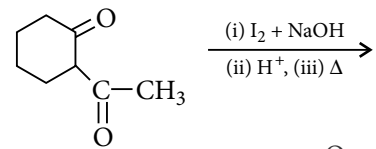
(d) 

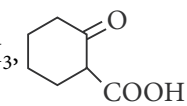
4. $CH_3CHO + 3HCHO \xrightarrow[I]{OH^-} (CH_2OH)_3CCHO$

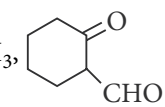
$\xrightarrow[II]{OH^-} (CH_2OH)_4C + (CH_2OH)_3CCOO^-$

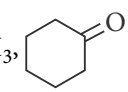
Reactions at stages I and II are respectively
(a) Cannizzaro, aldol
(b) aldol, aldol
(c) Cannizzaro, Cannizzaro
(d) aldol, Cannizzaro.

5. End products of the following sequence of reactions are



(a) yellow ppt. of CHI_3, 

(b) yellow ppt. of CHI_3, 

(c) yellow ppt. of CHI_3, 

(d) none of these.

6. An ester (*A*) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the compound, so formed, was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula, $C_9H_{10}O$ which gives iodoform test. The structure of (*A*) is

(a) $H_3C—OCOCH_2—C_6H_5$

(b) $C_2H_5COOC_6H_5$

(c) $C_6H_5COOC_2H_5$

(d) p-$H_3CO—C_6H_4—COCH_3$

7. An amine forms salt with BF_3 as,

Amine + $BF_3 \rightarrow$ [Amine $\rightarrow BF_3$].

If the alkyl group in amine is $CH_3—$, the order of basicity towards BF_3 is

(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$

(c) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

(d) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2$

8. Consider the following ions :

I. Me_2N—C$_6$H$_4$—$\overset{+}{N}\equiv N$

II. O_2N—C$_6$H$_4$—$\overset{+}{N}\equiv N$

III. CH_3O—C$_6$H$_4$—$\overset{+}{N}\equiv N$

IV. CH_3—C$_6$H$_4$—$\overset{+}{N}\equiv N$

The reactivity of these ions towards azo coupling reactions under similar conditions is

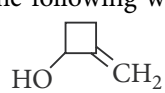
(a) I < IV < II < III (b) I < III < IV < II

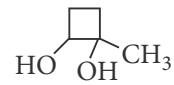
(c) III < I < II < IV (d) III < I < IV < II

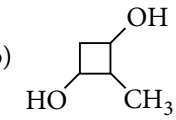
9. Phenol with carbon tetrachloride in presence of aqueous potassium hydroxide at 340 K followed by hydrolysis gives

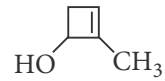
(a) acetylsalicylic acid (b) salicylaldehyde

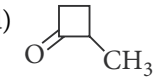
(c) salicylic acid (d) methyl salicylate.

10. Which one of the following will be the major product when  is heated with H_2SO_4 in the presence of $HgSO_4$?

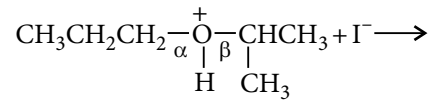
(a) 

(b) 

(c) 

(d) 

11. In the following reaction,

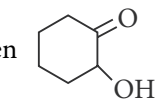


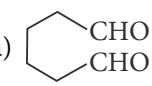
(a) α-bond is cleaved due to nucleophilic attack by I^- ion since, $(CH_3)_2CHOH$ is a weak base (a good leaving group)

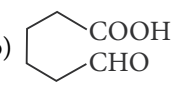
(b) β-bond is cleaved due to nucleophilic attack by I^- ion since, $CH_3CH_2CH_2OH$ is a weak base (a good leaving group)

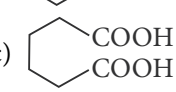
(c) α-bond is cleaved due to electrophilic attack of I^- ion.

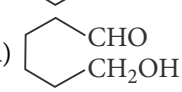
(d) β-bond is cleaved due to electrophilic attack of I^- ion.

12. The product obtained when  is oxidised with HIO_4 is

(a) 

(b) 

(c) 

(d) 

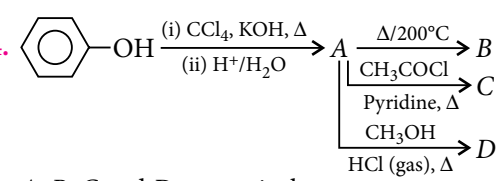
13. Butanenitrile may be prepared by heating

(a) propyl alcohol with alc. KCN

(b) butyl alcohol with alc. KCN

(c) butyl chloride with alc. KCN

(d) propyl chloride with alc. KCN.

14. 

A, *B*, *C* and *D* respectively are

(a) salicylic acid, salol, aspirin and oil of winter green

(b) salicylic acid, aspirin, salol and oil of winter green

(c) salicylic acid, oil of winter green, salol and aspirin

(d) none of the above.

15. 59 g of an amide obtained from a carboxylic acid, *R*COOH, upon heating with alkali liberated 17 g NH_3. The acid is

(a) formic acid (b) acetic acid

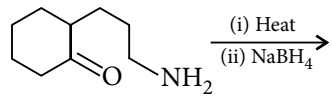
(c) propionic acid (d) benzoic acid.

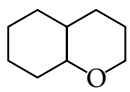
16. The rate of esterification of acetic acid with methyl alcohol (I), ethyl alcohol (II), isopropyl alcohol (III) and *tert*. butyl alcohol (IV) follows the order

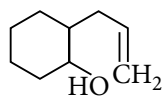
(a) I > II > III > IV (b) IV > III > II > I

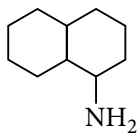
(c) II > I > IV > III (d) III > IV > I > II

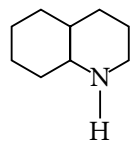
17. Identify the final product.



(a) 

(b) 

(c) 

(d) 

18. The red coloured compound formed during the Victor Meyer's test for ethyl alcohol is

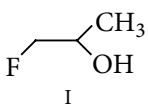
(a) $CH_3-\underset{\displaystyle NO_2}{\underset{|}{C}}=NO^-Na^+$

(b) $CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-NO_2^-Na^+$

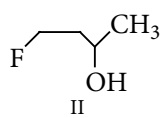
(c) $CH_3-\underset{\displaystyle NO}{\underset{|}{CH}}-NO_2$

(d) $(CH_3)_2\underset{\displaystyle NO_2}{\underset{|}{C}}-NO$

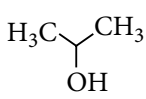
19. The order of reactivity of the following alcohols towards conc. HCl is



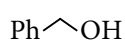
I



II



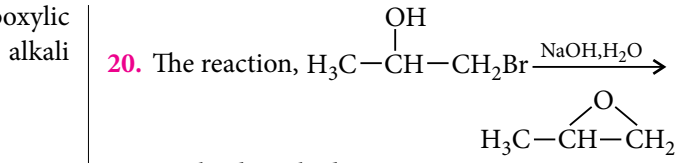
III



IV

(a) I > II > III > IV (b) IV > II > III > I

(c) IV > III > II > I (d) IV > III > I > II

20. The reaction, 

can be described as

(a) acid-base reaction followed by an intramolecular S_N1 reaction

(b) acid-base reaction followed by an intramolecular Williamson ether synthesis

(c) E 2 reaction followed by an addition reaction to a double bond

(d) S_N2 reaction following an intermolecular Williamson ether synthesis.

21. Which of the following is the strongest acid?

(a) 4-Nitrobenzoic acid

(b) 4-Methylbenzoic acid

(c) 4-Methoxybenzoic acid

(d) 4-Ethylbenzoic acid

22. Which of the following on oxidation with alkaline $KMnO_4$ followed by acidification with dilute HCl does not give benzoic acid?

(a) Toluene (b) Ethylbenzene

(c) Isopropylbenzene (d) *tert*-Butylbenzene

23. Which of the following will not be soluble in sodium bicarbonate?

(a) 2, 4, 6-Trinitrophenol

(b) Benzoic acid

(c) *o*-Nitrophenol

(d) Benzenesulphonic acid

24. An organic compound '*A*' has the molecular formula C_3H_6O. It undergoes iodoform test. When staturated with HCl it gives '*B*' of molecular formula $C_9H_{14}O$. '*A*' and '*B*' respectively are

(a) propanal and mesityl oxide

(b) propanol and mesityl oxide

(c) propanone and 2, 6-dimethyl-2,5-heptadien -4-one

(d) propanone and mesityl oxide

25. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed

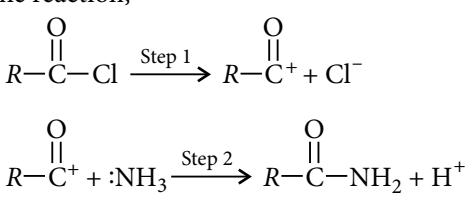
is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
(a) *p*-bromoaniline
(b) *p*-bromofluorobenzene
(c) 1, 3, 5-tribromobenzene
(d) 2, 4, 6-tribromofluorobenzene.

26. A compound '*A*' has a molecular formula C_7H_7NO. On treatment with Br_2 and KOH, '*A*' gives an amine '*B*' which gives carbylamine test. '*B*' upon diazotisation and coupling with phenol gives an azo dye. '*A*' can be
(a) $C_6H_5CH=NOH$
(b) $C_6H_5CONH_2$
(c) $C_6H_5CH_2NO$
(d) *o*, *m*- or *p*-$C_6H_4(NH_2)CHO$

27. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as
(a) iodide of Millon's base
(b) Hinsberg's reagent
(c) acetanilide
(d) Schiff's base.

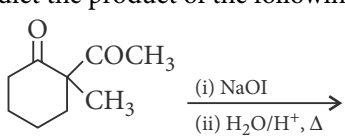
28. Which of the following diols would cleave into two fragments with HIO_4?
(a) 1, 3-Hexanediol (b) 2, 4-Hexanediol
(c) 1, 6-Hexanediol (d) 3, 4-Hexanediol

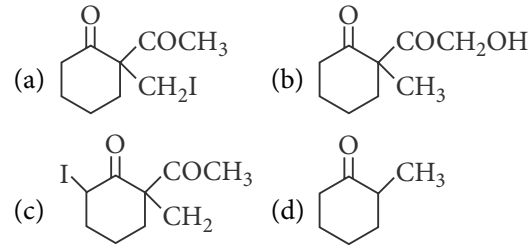
29. In the reaction,



step (2) is
(a) neutralisation
(b) electrophilic attack at the carbonyl carbon
(c) nucleophilic attack of lone pair of N at the carbonyl carbon leading to substitution
(d) nucleophilic addition reaction.

30. Predict the product of the following reaction.





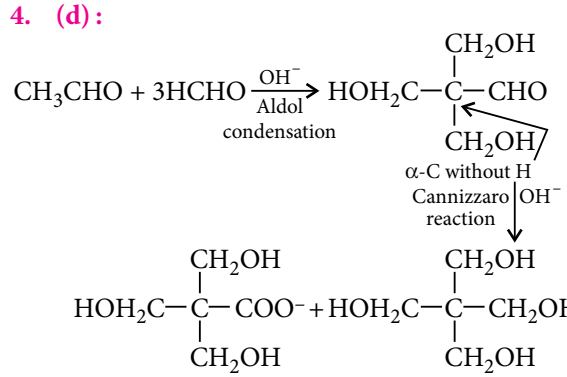
SOLUTIONS

1. **(a)**

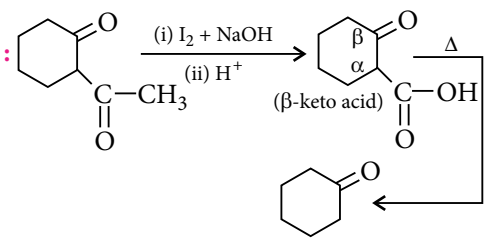
2. **(a) :** Since the compound ($C_4H_{10}O$) does not react with sodium, oxygen must be in the form of ether (*R*—O*R*). Further, since a single alkyl halide is formed, the two alkyl groups must be same, hence, ether is ethoxyethane ($C_2H_5OC_2H_5$).

3. **(a) :** *o*- and *p*-nitrophenols are stronger acids than *m*-nitrophenol. As a result, phenols (a) and (c) are stronger acids than (b) and (d). In (c), the $-NO_2$ group is flanked by two $-CH_3$ groups which push the $-NO_2$ group out of the plane of the benzene ring. As a result of this steric hindrance, the electron withdrawing resonance effect of the nitro group will be reduced and hence, the acidic character of the phenol will decrease. Therefore, phenol (a) is the strongest acid.

4. **(d) :**



5. **(c) :**

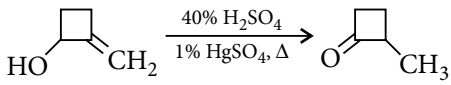


6. (a) **7.** (c)

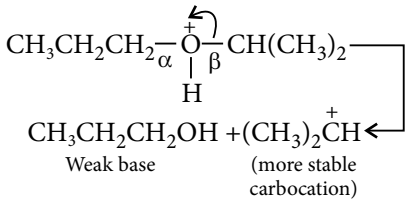
8. (b) : Less stable the diazonium salt, more reactive it is. Since the stability decreases in the order : I > III > IV > II, therefore, reactivity increases in the reverse order, *i.e.*, I < III < IV < II.

9. (c)

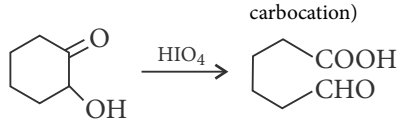
10. (d) :



11. (b) :



12. (b) :



13. (d) : $CH_3CH_2CH_2Cl$ + alc. KCN $\xrightarrow{100°C}$ $CH_3CH_2CH_2CN$ + KCl

14. (a)

15. (b) : $RCONH_2 + NaOH \rightarrow RCOONa + NH_3$

59 g (1 mole) 17 g (1 mole)

Thus, wt. of 1 mole of $RCONH_2$ = 59 g

In other words, $R + 12 + 16 + 14 + 2 = 59$

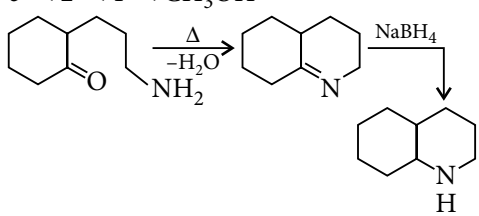
$\therefore R = 59 - 44 = 15$ g

Molecular mass of *R* is 15 which corresponds to CH_3 group, hence *R*COOH should be CH_3COOH.

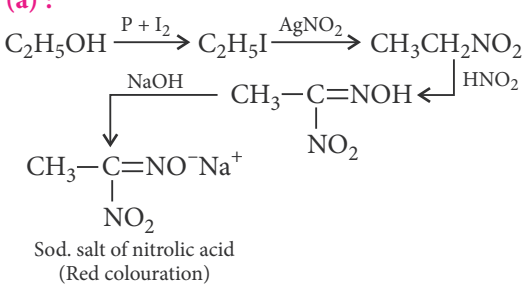
16. (a) : The reactivity of alcohols towards esterification increases as :

$3° < 2° < 1° < CH_3OH$

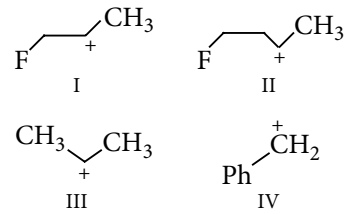
17. (d) :



18. (a) :



19. (c) : The reactivity of alcohols towards conc. HCl depends on the stability of carbocation being formed. When –OH group released as OH^- ion, carbocation is formed.



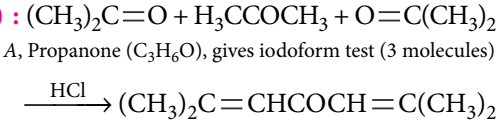
Thus, the order of stability of these carbocations is IV > III > II > I. Hence, the order of reactivity will also be same.

20. (b)

21. (a) : 4-Nitrobenzoic acid is the strongest acid as $-NO_2$ group shows *–I* and *–M* effects at *ortho* and *para* positions and it is a stronger electron withdrawing group.

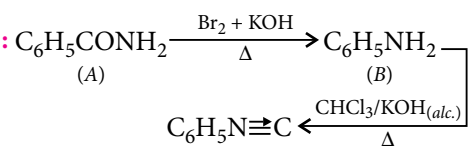
22. (d) **23.** (c)

24. (c) :



25. (d)

26. (b) :

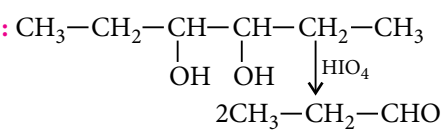


Aniline gives azo dye test.

27. (d) : $C_6H_5NH_2 + OHCC_6H_5 \xrightarrow[\Delta]{ZnCl_2}$ $C_6H_5N=CHC_6H_5$

This class of compounds is called Schiff's base or anils.

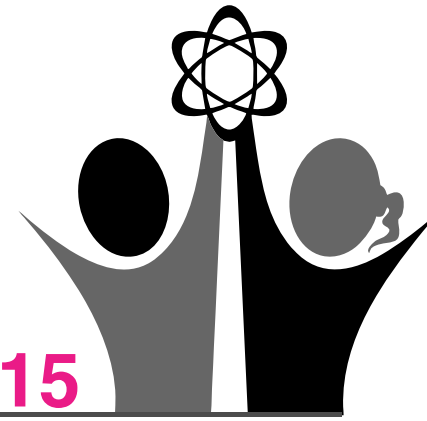
28. (d) :



Only vicinal diols are cleaved by HIO_4.

29. (c) **30.** (d)

CBSE BOARD



CHAPTERWISE PRACTICE PAPER 2015

Series-8

Amines and Biomolecules

Time : 3 hrs. **Marks** : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Question numbers 1 to 5 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 6 to 10 are short-answer questions and carry 2 marks each.
(iv) Question numbers 11 to 22 are also short-answer questions and carry 3 marks each.
(v) Question number 23 is value based question and carries 4 marks.
(vi) Question numbers 24 to 26 are long-answer questions and carry 5 marks each.
(vii) Use Log Tables, if necessary. Use of calculator is not allowed.

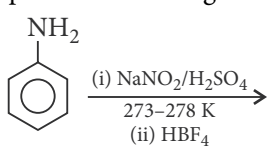
1. Give IUPAC name of sulphanilic acid.

2. Give an example of reducing and non-reducing sugar each.

3. Name the products formed when a nucleotide from DNA containing thymine is hydrolysed.

4. Trimethylamine and *n*-propylamine have the same molecular weight but the former boils at lower temperature than the latter. Give reason.

5. Complete the following reaction :



6. Distinguish between :
(i) Globular protein and fibrous protein
(ii) α-Glucose and β-glucose.

7. Arrange the following in increasing order of their basic strength :
(i) $C_2H_5NH_2, C_6H_5NH_2, NH_3, C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
(ii) Aniline, *p*-nitroaniline, *p*-toluidine.

8. Write the reaction
(i) which indicates the presence of five –OH groups in glucose molecule.
(ii) which indicates the presence of a primary alcoholic group in glucose.

9. Nitration of aniline gives *m*-nitroaniline in good yield although —NH_2 group is *o*,*p*-directing. Explain.

10. Write short notes on
(i) Carbylamine reaction
(ii) Hofmann bromamide reaction.

OR

What happens when
(i) Nitroethane is treated with $LiAlH_4$?
(ii) Benzenediazonium chloride reacts with phenol in basic medium?

11. What is the basic structural difference between starch and cellulose?

12. **(i)** Name the diseases caused due to the deficiency of
(a) vitamin K and
(b) vitamin A.

(ii) Why cannot vitamin C be stored in our body?

13. Account for the following :
(i) Ammonolysis of alkyl halide does not give a corresponding amine in pure state.
(ii) AgCl dissolves in aqueous methylamine solution.

14. Give reasons for the following :
(i) Aniline does not undergo Friedel–Crafts reaction.
(ii) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
(iii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

15. **(i)** Hormones are chemical messengers. Explain.
(ii) State the main function of insulin and adrenaline.

16. Complete the following reactions :
(i) $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow$
(ii) $C_6H_5N_2^+Cl^- + C_2H_5OH \rightarrow$
(iii) $C_6H_5NH_2 + Br_{2(aq)} \rightarrow$

17. How are the following reactions carried out? Write the equations and conditions.
(i) Acetic acid to ethylamine
(ii) Bromocyclohexane to cyclohexanamine.
(iii) Aniline to benzonitrile.

18. What is the difference between a nucleoside and a nucleotide?

19. Write short notes on
(i) Glycosidic linkage
(ii) Peptide linkage.

OR

Mention the type of linkage responsible for the formation of the following :
(i) Primary structure of protein.
(ii) Cross linkage of polypeptide chains.
(iii) α-helix formation.
(iv) β-sheet structure.

20. Account for the following observations :
(i) Sulphanilic acid is insoluble in water but is soluble both in aqueous bases and aqueous mineral acids.
(ii) Tertiary amines do not undergo acylation reaction.
(iii) Aniline readily reacts with bromine to give 2,4,6-tribromoaniline.

21. Give the structures of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN/KCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(iii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH/Br_2} B \xrightarrow[H_2O]{NaNO_2/HCl} C$

22. Define the following and give one example of each.
(i) Isoelectric point
(ii) Mutarotation
(iii) Enzymes

23. Rohan, had been complaining about stomach ache every now and then. His teacher called the parents and asked them to stop giving him junk food and include fibre and vitamin rich food like sprouts, fruits, whole wheat bread and green leafy vegetables in his diet plan.
(i) What values are expressed by the teacher?
(ii) Give two examples of water soluble vitamins.
(iii) What is the importance of fibre rich food?
(iv) Why do children need a protein rich diet?

24. (i) An optically active compound having molecular formula, $C_6H_{12}O_6$ is found in two isomeric forms (*A*) and (*B*) in nature. When (*A*) and (*B*) are dissolved in water they show the following equilibrium :

$$\underset{[\alpha]_D\ +111°}{(A)} \rightleftharpoons \underset{+52.2°}{\text{Equilibrium mixture}} \rightleftharpoons \underset{+19.2°}{(B)}$$

(a) What are such isomers called?
(b) Can they be called enantiomers? Justify your answer.
(c) What is invert sugar?

(ii) Give reasons for the following :
(a) Glucose and fructose give the same osazone.
(b) Amino acids are amphoteric in nature.

OR

(i) Answer the following questions briefly :
(a) What are the two good sources of vitamin A?
(b) What are reducing sugars?
(c) Why is vitamin C essential to us? Give its important sources.

(ii) Define the following terms in relation to proteins :
(a) Primary structure (b) Denaturation.

25. (i) Give one chemical test to distinguish between the following pairs of compounds:
(a) Methylamine and dimethylamine
(b) Secondary and tertiary amines

(ii) Write the chemical reaction stating the reaction conditions required for each of the following conversions :
(a) Methyl bromide to ethylamine
(b) Aniline to phenol
(c) *p*-Toluidine to 2-bromo-4-methylaniline

OR

(i) Write the chemical reaction stating the reaction conditions required for each of the following conversions :
(a) Aniline to chlorobenzene
(b) Acetaldehyde to ethylamine

(ii) Give one chemical test to distinguish between the following pairs of compounds:
(a) Ethylamine and aniline
(b) Aniline and benzylamine
(c) Aniline and *N*-methylaniline

26. (i) An organic compound (*A*) having molecular formula $C_2H_5O_2N$ on reduction gives a compound (*B*) with molecular formula C_2H_7N. (*B*) on treatment with HNO_2 gives (*C*) which gives positive iodoform test. Identify *A*.

(ii) Write the structures of the reagents/ organic compounds *A* to *F* in the following sequence of reactions :

$$A \xrightarrow[H_2SO_4(conc.)]{HNO_3(conc.)} B \xrightarrow{Sn/HCl} C \xrightarrow[Heat]{CHCl_3/KOH}$$

$$D \xrightarrow{H_2/Pt} E \xrightarrow{F} C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}-COCH_3 + CH_3CO_2H$$

OR

(i) An organic compound (*A*) with molecular formula $C_4H_{11}N$, capable of being resolved into optical isomers gives a base soluble product with benzenesulphonyl chloride. What is the structure and IUPAC name of (*A*)? What happens when this compound (*A*) is treated with acetyl chloride?

(ii) Which amine in each of the following pairs is a stronger base? Give reason.

(a) $CH_3-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-CH_3$ and $CH_3-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOCH_3$

(b) $CH_3CH_2CH_2NH_2$ and $CH_3NHCH_2CH_3$

SOLUTIONS

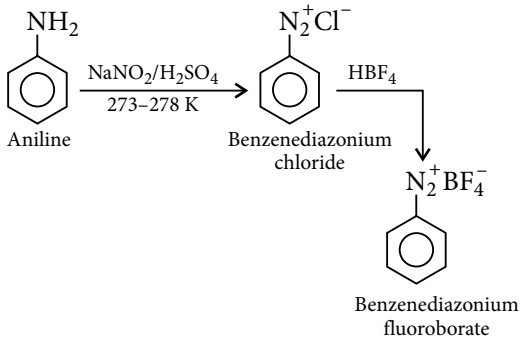
1. 4-Aminobenzenesulphonic acid

2. Reducing sugar – glucose
Non-reducing sugar – starch

3. The products of hydrolysis would be thymine, β-*D*-2-deoxyribose and phosphoric acid.

4. *n*-Propylamine has two H-atoms on N-atom and hence undergoes intermolecular H-bonding whereas trimethylamine being 3° amine does not undergo H-bonding.

5.

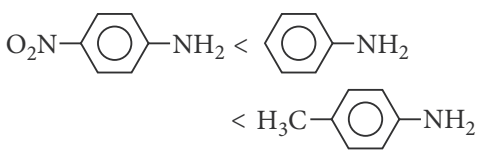


6. (i) Globular proteins are spherical in shape and are usually soluble in water whereas fibrous proteins have linear thread-like structure and are insoluble in water.

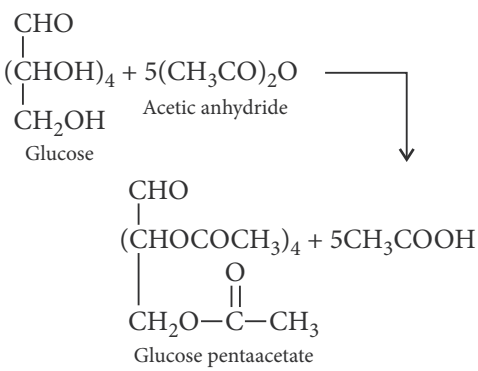
(ii) α-Glucose and β-glucose differ in configuration of –OH group on the anomeric carbon (C_1). In α-glucose, the –OH group at C_1 is towards right while in β-glucose, the –OH group at C_1 is towards left.

7. (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

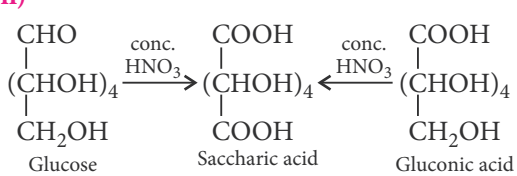
(ii)



8. (i)



(ii)



9. Although $-NH_2$ is *o*, *p*-directing group but in case of nitration, aniline is protonated to become anilinium ion which is *meta* directing. Hence, *m*-nitroaniline is obtained in good yield.

10. (i) **Carbylamine reaction :** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.

$$R—NH_2 + CHCl_3 + 3KOH_{(alc.)} \xrightarrow{\text{Heat}} R—NC + 3KCl + 3H_2O$$

Carbylamine (foul smell)

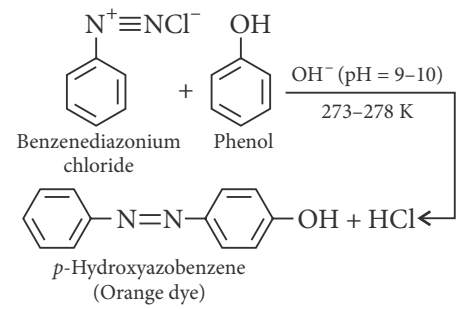
(ii) **Hofmann bromamide reaction :** Primary amines when heated with Br_2 and aqueous or ethanolic solution of NaOH lose a carbon atom and are converted to the corresponding amines.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} 2H_2O + Na_2CO_3 + 2NaBr + \underset{\text{Methylamine}}{CH_3NH_2}$$

OR

(i) $\underset{\text{Nitroethane}}{C_2H_5NO_2} \xrightarrow[\text{dry ether}]{LiAlH_4} \underset{\text{Ethylamine}}{C_2H_5—NH_2} + 2H_2O$

(ii)



11. The basic structural difference between starch and cellulose is of linkage between the glucose units. In starch, there is α-*D*-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymers of α-*D*-glucose. Amylose is water soluble component which constitutes about 15–20% of starch. Chemically amylose is a long unbranched chain with 200–1000 α-*D*-(+)-glucose units held by C_1–C_4 glycosidic linkage.

Amylopectin is insoluble in water and constitites about 80–85% of starch. It may contain 2000 – 3000 glucose units. It is a branched chain polymer of α-*D*-glucose units in which chain is formed by C_1–C_4 glycosidic linkage whereas branching occurs by C_1–C_6 glycosidic linkage. On the other hand, cellulose is a linear polymer of β-*D*-glucose in which C_1 of one glucose unit is connected to C_4 of the other through β-*D*-glycosidic linkage.

12. (i) (a) Deficiency of vitamin K causes impaired blood clotting.

(b) Deficiency of vitamin A causes xerophthalmia.

(ii) Vitamin C is a water soluble vitamin. Water soluble vitamins when supplied regularly in the diet cannot be stored in our body because they are readily excreted in urine.

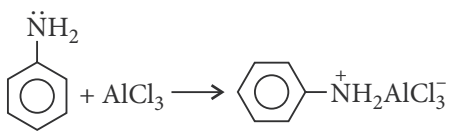
13. (i) During ammonolysis, 1° amines obtained behave as nucleophiles and can further react with alkyl halides to form secondary and tertiary amines and finally quaternary ammonium salt.

$$R{-}X + \ddot{N}H_3 \longrightarrow R\ddot{N}H_2 \xrightarrow{RX} R_2\ddot{N}H \xrightarrow{RX} R_3\ddot{N} \xrightarrow{RX} R_4\overset{+}{N}X^-$$

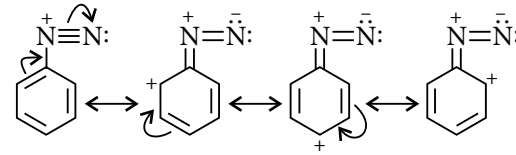
(ii) AgCl dissolves in aqueous methylamine solution due to formation of complex compound.

$$AgCl + 2CH_3NH_2 \rightarrow [Ag(CH_3NH_2)_2]^+Cl^-$$

14. (i) In Friedel–Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge and acts as a strong deactivating group, hence aniline does not undergo Friedel–Crafts reaction.



(ii) Diazonium salts of aromatic amines are more stable due to the dispersal of the positive charge over the benzene ring. As a result C—N bond acquires some double bond character.



(iii) Gabriel phthalimide synthesis involves the nucleophilic attack on alkyl halide and during the reaction, the alkyl group attaches to the attacking nitrogen atom. Since further attack on a second molecule of alkyl halide is not possible, so pure primary amines are formed in this reaction without any impurity of 2° and 3° amines.

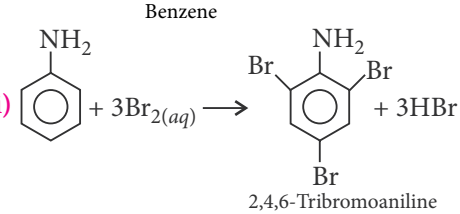
15. (i) Hormones are molecules that transfer information from one group of cells to distant tissues or organ and thus control the metabolism. So, they act as chemical messengers.

(ii) Insulin controls the level of glucose in blood and adrenaline prepares animals and humans for emergency in many ways by raising the pulse rate and blood pressure, etc.

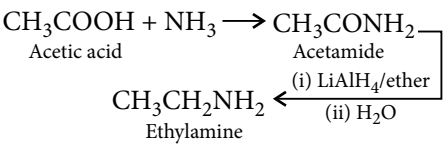
16. (i)
$$C_6H_5\overset{+}{N}_2Cl^- + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$$

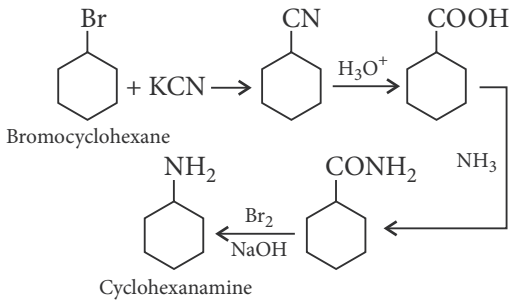
(ii)
$$C_6H_5\overset{+}{N}_2Cl^- + C_2H_5OH \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + CH_3CHO + HCl$$

(iii)

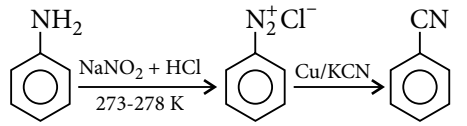


17. (i)





(ii)

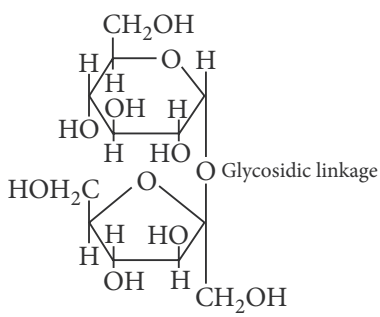


18. Nucleoside is formed by condensation of a purine or pyrimidine base with pentose sugar at 1′ position. When nucleoside is linked to phosphoric acid at 5′ position of sugar moiety, a nucleotide is formed.

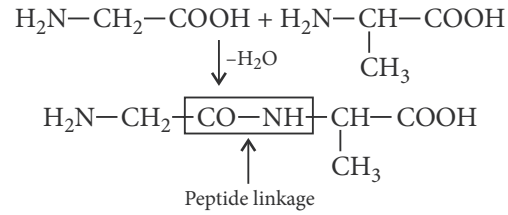
(i) Nucleoside has two units - pentose sugar and a nitrogenous base.

(ii) Nucleotide has three units - phosphate group, pentose sugar and a nitrogenous base.

19. (i) **Glycosidic linkage :** The two monosaccharide units are joined together through an oxide linkage formed by loss of a molecule of H_2O. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.



(ii) **Peptide linkage :** A peptide bond is an amide linkage formed between –COOH group of one α-amino acid and $–NH_2$ group of the other α-amino acid by loss of a water molecule.



OR

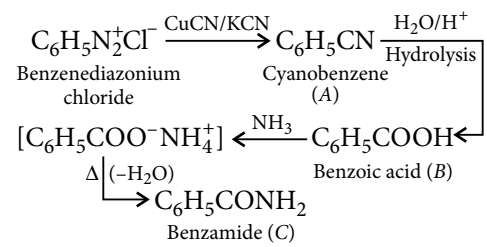
	Biomolecule	Type of linkage
(i)	Primary structure of protein	Peptide bond (linkage)
(ii)	Cross linkage of polypeptide chains	Hydrogen bonds disulphide linkages, van der Waals and electrostatic forces of attraction
(iii)	α-helix formation	Intramolecular hydrogen bonds
(iv)	β-sheet structure	Intermolecular hydrogen bonds

20. (i) Sulphanilic acid forms Zwitter ion therefore, it is soluble both in bases and mineral acids but is insoluble in water due to greater hydrocarbon part due to which it cannot form H-bonds with water.

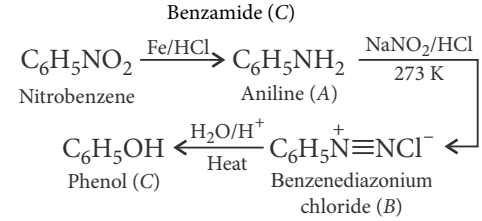
(ii) Tertiary amines do not undergo acylation reaction because they do not have nitrogen attached to hydrogen.

(iii) In Aniline, $—NH_2$ group is electron releasing, therefore, it increases electron density at *o* and *p*-positions, and forms 2, 4, 6-tribromoaniline.

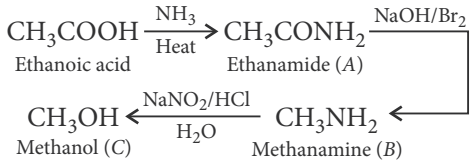
21. (i)



(ii)



(iii)



22. (i) **Isoelectric point :** The pH at which there is no net migration of the amino acid under the influence of an applied electric field is called isoelectric point. *e.g.*,

Amino acid	Isoelectric point
Neutral	pH = 5 – 6.3
Acidic	pH = 3 – 5.4
Basic	pH = 7.6 – 10.8

(ii) **Mutarotation :** It is the spontaneous change in optical rotation when an optically active substance is dissolved in water, *e.g.*, α-glucose, when dissolved in water, its optical rotation changes from +111° to +52.5°.

(iii) **Enzymes :** They are biological catalysts which catalyse specific biochemical reactions, *e.g.*,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{D\text{-Glucose}}{C_6H_{12}O_6} + \underset{D\text{-Fructose}}{C_6H_{12}O_6}$$

23. (i) Teacher has expressed her responsibility and concern about the health of children.

(ii) Vitamin B complex and vitamin C.

(iii) Fibre rich food prevents constipation which is responsible for many other problems.

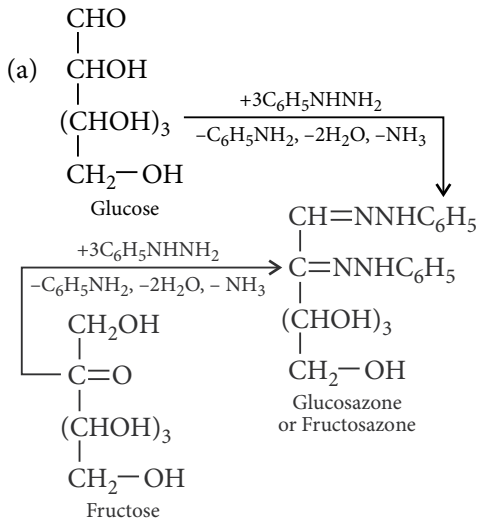
(iv) Children require protein rich diet to build muscles for the growth.

24. (i) (a) These are called anomers.

(b) They cannot be called enantiomers as they are not the mirror images of each other.

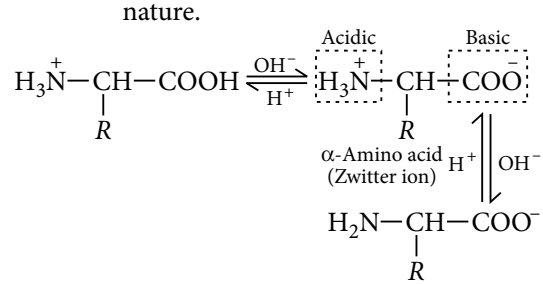
(c) The laevorotatory mixture of *D*-(+)-glucose and *D*-(–)-fructose obtained by the hydrolysis of sucrose is known as invert sugar.

(ii) (a)



During osazone formation, the reaction occurs only at C_1 and C_2. As glucose and fructose differ from each other only in the arrangement of atoms at C_1 and C_2, therefore they give the same osazone.

(b) Since amino acids have both acidic ($-\overset{+}{N}H_3$) as well as basic ($-\overset{-}{C}OO$) groups, therefore, they are amphoteric in nature.



OR

(i) (a) Two good sources of vitamin A are carrots and butter.

(b) All those carbohydrates which contain free aldehyde or ketone group and reduce Tollens' reagent or Fehling's solution are known as reducing sugars.

(c) Vitamin C is essential for us because its deficiency causes scurvy (bleeding gums) and pyorrhea (loosening and bleeding of teeth). Its sources are citrus fruits, *amla*, green leafy vegetables.

(ii) (a) **Primary structure :** The specific sequence in which the various α-amino acids present in a protein are linked to one another is called its primary structure.

(b) **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of native structure of protein is called denaturation.

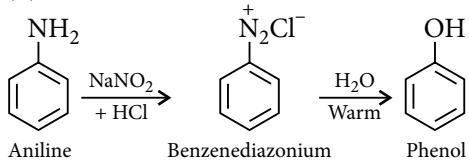
25. (i) (a) Methylamine and dimethylamine can be distinguished by carbylamine test. Methylamine, a primary amine, gives offensive smell on heating with chloroform and alcoholic solution of KOH whereas dimethylamine does not react.

(b) Secondary amine reacts with benzenesulphonyl chloride to form *N*,*N*-dialkylbenzenesulphonamide which is insoluble in KOH. Tertiary amine does not react.

(ii) (a) $CH_3Br \xrightarrow[\Delta]{\text{Alc. KCN}} CH_3CN \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2NH_2$

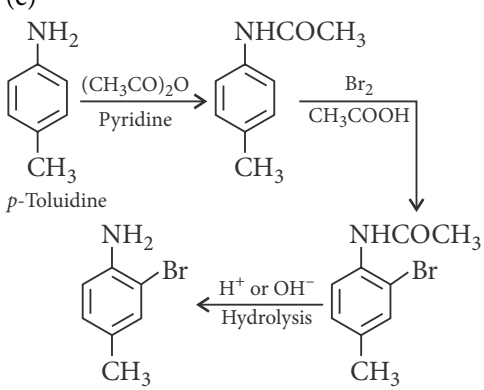
Methyl bromide — Ethylamine

(b)



Aniline — Benzenediazonium chloride — Phenol

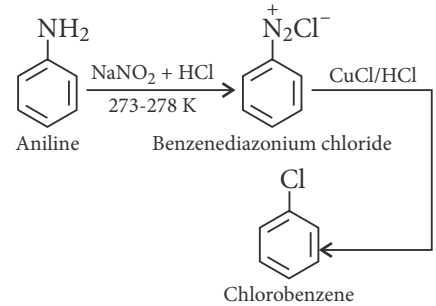
(c)



p-Toluidine — 2-Bromo-4-methylaniline

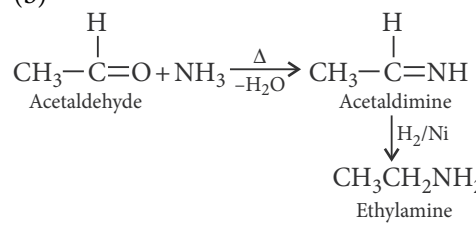
OR

(i) (a)



Aniline — Benzenediazonium chloride — Chlorobenzene

(b)



Acetaldehyde — Acetaldimine — Ethylamine

(ii) (a) Ethylamine and aniline can be distinguished by azo dye test. Aniline reacts with HNO_2 at 273-278 K followed by treatment with an alkaline solution of 2-naphthol and gives a brilliant orange or red coloured dye.

Ethylamine does not form dye. It will give brisk effervescene due to the evolution of N_2 but solution remains clear.

(b) Aniline and benzylamine can also be distinguished by azo dye test. Aniline gives azo dye test while benzylamine does not.

(c) Aniline when heated with an alcoholic solution of KOH and $CHCl_3$ gives offensive smell of phenyl isocyanide while *N*-methylaniline being a secondary amine does not give this test.

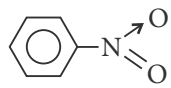
26. (i) $\underset{(A)}{CH_3CH_2NO_2} \xrightarrow{Sn/HCl} \underset{(B)}{CH_3CH_2NH_2}$

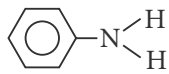
$\underset{(B)}{CH_3CH_2NH_2} + HNO_2 \rightarrow \underset{(C)}{CH_3CH_2OH} \xrightarrow{I_2/NaOH} CHI_3$

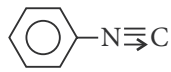
Iodoform

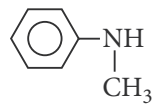
(ii) Structures of reagents/organic compounds:

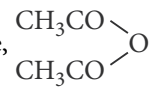
A = Benzene, 

B = Nitrobenzene, 

C = Aniline, 

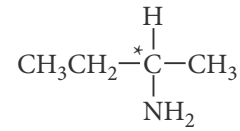
D = Phenyl isocyanide, 

E = Methyl phenyl amine, 

F = Acetic anhydride, 

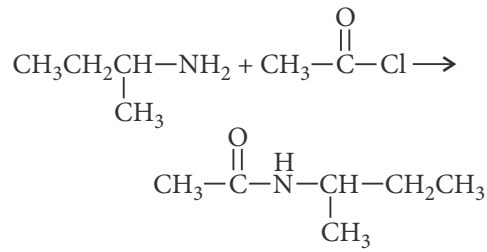
OR

(i) As compound (*A*) is giving a base soluble product with Hinsberg's reagent, it means the compound is a primary amine with $-NH_2$ group. As the compound is capable of being resolved into optical isomers, it indicates the presence of chiral carbon. Therefore, the structure of compound (*A*) is



2-Butanamine

With acetyl chloride, compound (*A*) forms amide.



(ii) (a) $CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$ is more basic than $CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOCH_3$ because $-COOCH_3$ is an electron withdrawing group which decreases the electron density on nitrogen atom.

(b) Since 2° amines are more basic than 1° amines, so, $CH_3NHCH_2CH_3$ is more basic than $CH_3CH_2CH_2NH_2$. Because in 2° amine there are two electron releasing groups and in 1° amine only one electron releasing group is present.

EXAMINER'S MIND CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. Among the following, the compound that is both paramagnetic and coloured is
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2[TiCl_6]$
(c) $VOSO_4$ (d) $K_3[Cu(CN)_4]$

2. Aldol condensation between which of the following compounds followed by dehydration gives methyl vinyl ketone?
(a) Methanal and ethanal
(b) Two moles of formaldehyde
(c) Methanal and propanone
(d) Two moles of ethanal

3. *tert*-Butyl bromide on treatment with sodium methoxide yields
(a) sodium tertiary butoxide
(b) *tert*-butyl methyl ether
(c) *tert*-butyl alcohol
(d) isobutylene.

4. In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one-eighth of tetrahedral voids are occupied by divalent cations '*A*' while one-half of octahedral voids are occupied by trivalent cations '*B*'. The formula of the oxide is
(a) A_2BO_4 (b) AB_2O_3
(c) A_2BO_3 (d) AB_2O_4

5. Aniline is treated with $NaNO_2$/HCl at 0°C to give compound *X* which on treatment with cuprous cyanide gives another compound *Y*. When compound *Y* is treated with H_2/Ni compound *Z* is obtained. Compound *Z* is
(a) benzyl alcohol (b) benzylamine
(c) *N*-ethylaniline (d) phenol.

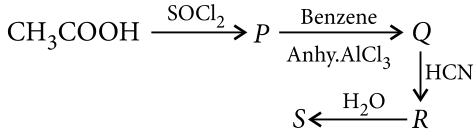
6. Aqueous solution of nickel sulphate on treating with pyridine and then adding a solution of sodium nitrate gives dark blue crystals of
(a) $[Ni(py)_4]SO_4$
(b) $[Ni(py)_2(NO_2)_2]$
(c) $[Ni(py)_4](NO_2)_2$
(d) $[Ni(py)_3(NO_2)]_2SO_4$

7. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.

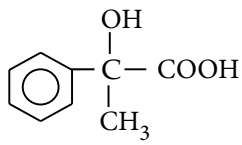
8. Which of the following statements are incorrect?
(i) Resins are thermoplastics.
(ii) Nylon-6 is an example of addition homopolymers.
(iii) Neoprene is a synthetic rubber.
(iv) Buna-S is a polymer of 1, 3-butadiene and acrylonitrile.
(a) (i), (iii), (iv) (b) (ii), (iii)
(c) (i), (ii), (iv) (d) All are incorrect.

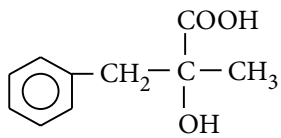
9. For the dilute solution, Raoult's law states that
(a) the lowering of vapour pressure is equal to the mole fraction of the solution
(b) the relative lowering of vapour pressure is equal to the mole fraction of the solute
(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution
(d) the vapour pressure of the solution is equal to the mole fraction of solvent.

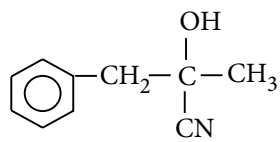
10. In a set of reactions, acetic acid yields a product *S*.

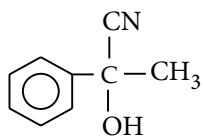


The compound *S* would be

(a) 

(b) 

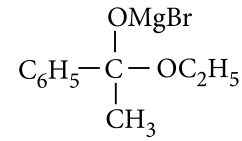
(c) 

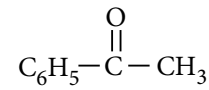
(d) 

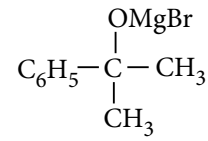
11. Which of the following statements about lanthanides is incorrect?
(a) All lanthanides are highly dense metals.
(b) More characteristic oxidation state of lanthanides is +3.
(c) Lanthanides are separated from one another by ion exchange method.
(d) Ionic radii of trivalent lanthanides steadily increase with increase in atomic number.

12. The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA?
(a) 1st (b) 2nd
(c) 3rd (d) 4th

13. Which of the following are intermediates in the reaction of excess of CH_3MgBr with $C_6H_5COOC_2H_5$ to make 2-phenyl-2-propanol?

A. 

B. 

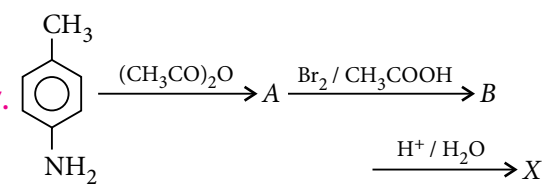
C. 

(a) A and B (b) A, B and C
(c) A and C (d) B and D

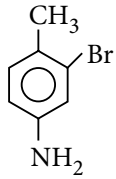
14. For a first-order reaction, the time required for 99.9% of the reaction to take place is nearly
(a) 10 times that required for half the reaction
(b) 100 times that required for two-third of the reaction
(c) 10 times that required for one-fourth of the reaction
(d) 20 times that required for half of the reaction.

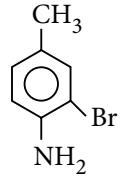
15. Calculate the ebullioscopic constant for water. The heat of vaporisation is 40.685 kJ mol^{-1}.
(a) 0.512 K kg mol^{-1} (b) 1.86 K kg mol^{-1}
(c) 5.12 K kg mol^{-1} (d) 3.56 K kg mol^{-1}

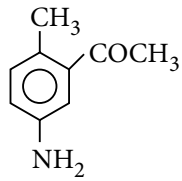
16. Antiseptic chloroxylenol is
(a) 4-chloro-3,5-dimethylphenol
(b) 3-chloro-4,5-dimethylphenol
(c) 4-chloro-2,5-dimethylphenol
(d) 5-chloro-3,4-dimethylphenol.

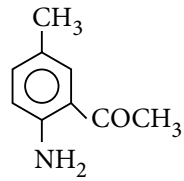
17. 

What is *X* ?

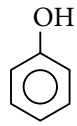
(a) 

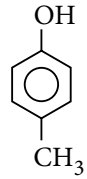
(b) 

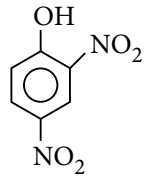
(c) 

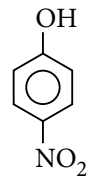
(d) 

18. Strength of acidity is in order

I. 

II. 

III. 

IV. 

(a) II > I > III > IV (b) III > IV > I > II
(c) I > IV > III > II (d) IV > III > I > II

19. For H_3PO_3 and H_3PO_4 the correct choice is
(a) H_3PO_3 is dibasic and reducing
(b) H_3PO_3 is dibasic and non-reducing
(c) H_3PO_4 is tribasic and reducing
(d) H_3PO_3 is tribasic and non-reducing.

20. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is
(a) Na_2SO_4 (b) $CaCl_2$
(c) $Al_2(SO_4)_3$ (d) NH_4Cl

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. The half-cell (electrode) reactions with their appropriate standard reduction potentials are :
(i) $Pb^{2+} + 2e^- \rightleftharpoons Pb$ ($E^\circ = -0.13$ V)
(ii) $Ag^+ + e^- \rightleftharpoons Ag$ ($E^\circ = +0.80$ V)
In the light of the data given, which of the following reaction(s) will take place?
(a) $Pb^{2+} + 2Ag \rightarrow 2Ag^+ + Pb$
(b) $Pb^{2+} + H_2 \rightarrow 2H^+ + Pb$
(c) $2H^+ + 2Ag \rightarrow 2Ag^+ + H_2$
(d) $2Ag^+ + Pb \rightarrow Pb^{2+} + 2Ag$

22. A positive carbylamine test is given by
(a) *N*, *N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine.

23. Potassium manganate (K_2MnO_4) is formed when
(a) chlorine is passed into aqueous $KMnO_4$ solution
(b) manganese dioxide is fused with potassium hydroxide in air
(c) formaldehyde reacts with potassium permanganate in presence of a strong alkali
(d) potassium permanganate reacts with concentrated sulphuric acid.

24. Which of the following synthesis gives 3-methyl-1-hexanol?
(a) 2-Bromohexane $\xrightarrow[\text{dry ether}]{\text{Mg}}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) HCHO}}$
(b) 2-Bromopentane $\xrightarrow[\text{dry ether}]{\text{Mg}}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } \triangle O}$
(c) 3-Bromopentane $\xrightarrow[\text{dry ether}]{\text{Mg}}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3CHO}$
(d) 1-Bromobutane $\xrightarrow[\text{dry ether}]{\text{Mg}}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3COCH_3}$

25. Adsorption is accompanied by
(a) decrease in enthalpy of the system
(b) increase in entropy of the system
(c) decrease in free energy of the system
(d) $T\Delta S$ for the process is positive.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph.

Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. The extraction and isolation of metals from ores involve the following major steps :

- Concentration of the ore.
- Isolation of the metal from its concentrated ore.
- Purification of the metal.

26. According to Ellingham diagram, the oxidation reaction of carbon to carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature?

(a) Al_2O_3 (b) Cu_2O
(c) MgO (d) ZnO

27. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are

(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively.

28. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

	Cathode	Anode
(a)	pure zinc	pure copper
(b)	impure sample	pure copper
(c)	impure zinc	impure sample
(d)	pure copper	impure sample.

Paragraph for Questions 29 to 31

Nucleophilic substitution reactions in haloalkanes proceed by two different mechanisms :

- Substitution nucleophilic bimolecular (S_N2)
- Substitution nucleophilic unimolecular (S_N1)

A S_N2 reaction proceeds with complete stereochemical inversion while a S_N1 reaction proceeds with racemisation.

29. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is

(a) 2 (b) 3
(c) 4 (d) 1

30. The reactions

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

$$CH_3(CH_2)_5\underset{\displaystyle H}{\overset{\displaystyle H_3C}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow{OH^-} HO-\underset{\displaystyle H}{\overset{\displaystyle (CH_2)_5CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + Br^-$$

obey the mechanism predominantly

(a) S_N1 (b) S_N2
(c) S_E1 (d) S_E2

31. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction is

(a) CH_3Cl (b) $(C_2H_5)_2CHCl$
(c) $(CH_3)_3CCl$ (d) $(CH_3)_2CHCl$

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists :

	List I Compounds	List II pK_b value
P.	Ammonia	1. 8.92
Q.	Methanamine	2. 9.38
R.	Benzenamine	3. 3.38
S.	*N*, *N*-Dimethylaniline	4. 4.75

	P	Q	R	S
(a)	2	1	3	4
(b)	1	2	3	4
(c)	4	1	2	3
(d)	4	3	2	1

33. Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	1 mole of Al^{3+} to Al	1.	482500 C
Q.	1 mole of MnO_4^- to Mn^{2+}	2.	96500 C
R.	1 mole of H_2O to O_2	3.	289500 C
S.	1 mole of FeO to Fe_2O_3	4.	193000 C

	P	Q	R	S
(a)	3	4	2	1
(b)	3	1	4	2
(c)	1	3	2	4
(d)	4	3	1	2

34. Match the List I with List II and select the correct answer using the code given below the lists :

	List I Interhalogen compounds		List II Shape
P.	XY	1.	T-shaped
Q.	XY_3	2.	Square pyramidal
R.	XY_5	3.	Linear
S.	XY_7	4.	Pentagonal bipyramidal

	P	Q	R	S
(a)	1	2	4	3
(b)	4	3	1	2
(c)	3	1	2	4
(d)	4	1	2	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

35. Assertion : The total number of isomers shown by $[Co(en)_2Cl_2]^+$ complex ion is three.

Reason : $[Co(en)_2Cl_2]^+$ complex ion has an octahedral geometry.

36. Assertion : Both SO_2 and SO_3 are reducing agents.

Reason : Both SO_2 and SO_3 bleach the articles by reduction.

37. Assertion : Heat of chemisorption is always greater than heat of physisorption.

Reason : Chemisorption involves stronger bonds than physisorption.

38. Assertion : Bakelite is a thermosetting plastic.

Reason : In thermosetting plastics, the polymeric chains are held together by strong ionic bonds.

39. Assertion : The cell constant of a cell does not depend upon the nature of the material of the electrode.

Reason : The observed conductance of a solution depends upon the nature of the material of the electrodes.

40. Assertion : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is available for resonance.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. A binary solid (A^+B^-) has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solids is AB_x. The value of x is

42. Of the following compounds methanal, 2-methylpentanal, benzaldehyde, benzophenone, cyclohexanone, 1-phenylpropanone, phenylacetaldehyde, butan-1-ol and 2, 2-dimethylbutanal, the total number of compounds that can undergo aldol condensation is

43. In the complex, $[Fe(EDTA)]^-$, the coordination number of the metal ion is

44. Time required to complete a definite fraction of a reaction varies inversely to the concentration of reactant, then the order of reaction is

45. When Cl_2 is passed through hot and concentrated solution of KOH, the compound formed is $KClO_x$. The value of x is

46. The total number of optically active compounds from the following list is

$C_2H_5NHCH_3$,

$CH_3CH_2CH(CH_3)N(CH_3)C_2H_5$,

$[Ph(CH_3)(C_2H_5)\overset{+}{N}HI]^-$,

$[(C_2H_5)(CH_3)_2\overset{+}{N}H]I^-$,

$C_6H_5(CH_3)(C_2H_5)\overset{+}{N}-O^-$,

$(CH_3)(C_2H_5)NCH(CH_3)_2$

47. If 0.15 g of a solute dissolved in 15 g of solvent is boiled at a temperature higher by 0.216 °C, than that of the pure solvent, the molecular weight of the substance is 1×10^x g. The value of x is (Molal elevation constant for the solvent is 2.16 °C)

48. Total number of isomers of $C_5H_{11}Cl$ is (optical isomers not included.)

49. van't Hoff factor of $Hg_2(NO_3)_2$ if it is 100% ionised in aqueous solution is

50. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and EMF of the cell set-up was 0.62 V.

$Pt_{(s)}, H_{2(g)} |H^+ (1\ M)|| Ag^+_{(aq)}|Ag_{(s)}$

The percentage of Ag in the alloy is

$[E^\circ_{cell} = 0.80\ V, 2.303\ RT/F = 0.06$ at 25 °C]

SOLUTIONS

1. **(c) :** $K_2Cr_2O_7 \rightarrow Cr^{+6} : 3d^0$

$(NH_4)_2[TiCl_6] \rightarrow Ti^{+4} : 3d^0$

$VOSO_4 \rightarrow V^{+4} : 3d^1$

$K_3[Cu(CN)_4] \rightarrow Cu^+ : 3d^{10}$

2. **(c) :** $\underset{\text{Methanal}}{HCHO} + \underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\text{dil. NaOH}}$

$H_2C(OH)-CH_2-C(=O)-CH_3 \xrightarrow[-H_2O]{\Delta}$

$CH_2=CH-CO-CH_3$

Methyl vinyl ketone

3. **(d) :** Tertiary alkyl halides would undergo elimination to produce alkenes. Thus, *tert*-butyl bromide on heating with methoxide ion mainly undergoes elimination to form isobutylene.

4. **(d) :** No. of oxide ions (O^{2-}) per unit cell = 1

No. of tetrahedral voids per ion in lattice = 2

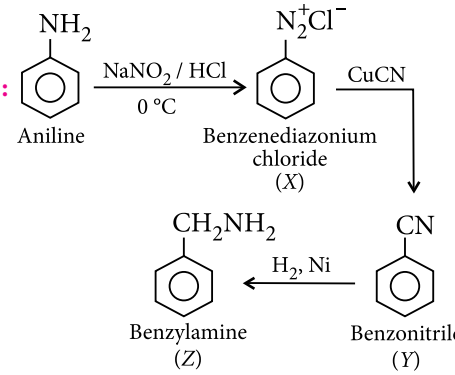
No. of divalent cations (A) = $\frac{1}{8} \times 2 = \frac{1}{4}$

No. of octahedral voids per ion in lattice = 1

No. of trivalent cations (B) = $1 \times \frac{1}{2} = \frac{1}{2}$

Hence, Formula = $A_{1/4}B_{1/2}O = AB_2O_4$

5. **(b) :**

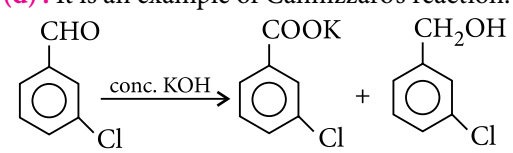


Aniline → Benzenediazonium chloride (X) → Benzylamine (Z) / Benzonitrile (Y)

6. **(c) :** $NiSO_4 + 4py + 2NaNO_2 \longrightarrow Na_2SO_4 + [Ni(py)_4](NO_2)_2$

Blue

7. **(d) :** It is an example of Cannizzaro's reaction.

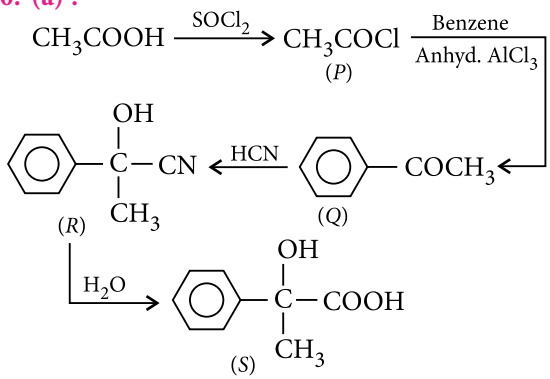


m-chlorobenzaldehyde → Potassium *m*-chlorobenzoate + *m*-chlorobenzyl alcohol

8. **(c) :** Resins are thermosetting plastics. Nylon-6 is an example of condensation homopolymers. Buna-S is a polymer of 1,3-butadiene and styrene.

9. (b)

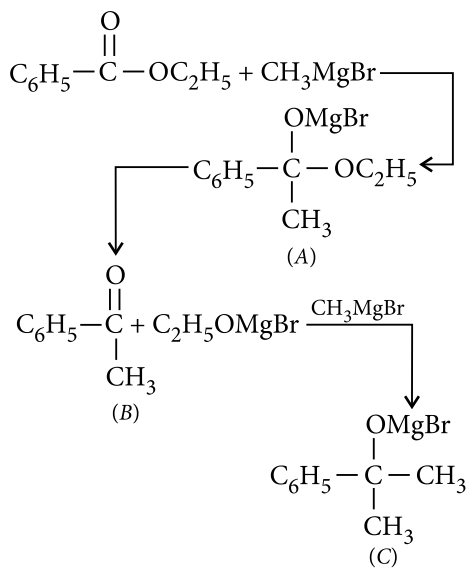
10. (a) :



11. (d) : Ionic radii of trivalent lanthanides steadily decrease with increase in atomic number due to lanthanide contraction.

12. (b) : The sugar molecule found in RNA is *D*-ribose while the sugar molecule in DNA is *D*-2-deoxyribose. The sugar *D*-2-deoxyribose differs from ribose only in the substitution of hydrogen for an — OH group at 2-position.

13. (b) :



14. (a) : $k = \frac{1}{t}\ln\frac{100}{100-99.9} = \frac{1}{t}\ln\frac{100}{0.1}$

or $\frac{\ln 2}{t_{1/2}} = \frac{1}{t}\ln 10^3 \left(\therefore k = \frac{\ln 2}{t_{1/2}}\right)$

or $\frac{\log 2}{t_{1/2}} = \frac{1}{t}\times\log 10^3 = \frac{3}{t}$

$$t_{1/2} = \frac{\log 2}{3}\times t = \frac{0.3010}{3}\times t = 0.10t$$

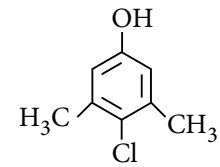
$\therefore \quad t = 10t_{1/2}$

15. (a) : $K_b = \frac{RT_0^2 M}{1000\Delta H_{vapour}}$

$$= \frac{8.314\times(373.15)^2\times 18}{1000\times 40.685}\times 10^{-3}$$

$= 0.512$ K kg mol^{-1}

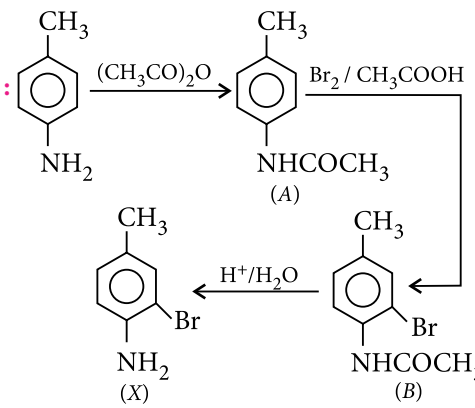
16. (a) :



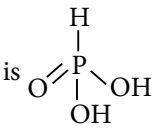
Chloroxylenol

(4-Chloro-3,5-dimethylphenol)

17. (b) :



18. (b) : An electron withdrawing group increases the acidic strength while an electron releasing group decreases the acidic strength of phenol.

19. (a) : Structure of H_3PO_3 is 

Since it has only two —OH groups so it is dibasic and it has one P — H bond so it is reducing.

20. (c) : Sb_2S_3 is a negative sol and according to Hardy- Schulze rule :

(i) Ions carrying charge opposite to that of sol particles are effective in causing coagulation.

(ii) Coagulating power of an electrolyte is directly proportional to the valency of the active ions.

∴ Out of the given options, the most effective coagulating agent is $Al_2(SO_4)_3$ or Al^{3+} ion.

21. (d) : $Ag^+ + e^- \rightleftharpoons Ag(E^\circ = +0.80\ V)$ – at cathode

$Pb \rightleftharpoons Pb^{2+} + 2e^-\ (E^\circ = +0.13\ V)$ – at anode

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = 0.80 - 0.13$

$E^\circ_{cell} = 0.67\ V$

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative

$\Delta G^\circ = -nFE^\circ_{cell}$

When E°_{cell} is positive, the cell reaction is spontaneous and serves as a source of electrical energy.

22. (b,d) : Both aliphatic and aromatic primary amines give positive carbylamine test. Hence, 2,4-dimethylaniline and *p*-methylbenzylamine give this test.

23. (b,c): $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

$HCHO + 2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + HCOOH$

24. (b) : $CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow[dry\ ether]{Mg}$

$CH_3-\underset{\underset{MgBr}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow{\triangle O}$

$CH_3-\underset{\underset{CH_2CH_2OMgBr}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow{H_3O^+}$

$CH_3-\underset{\underset{CH_2CH_2OH}{|}}{CH}-CH_2-CH_2-CH_3$

25. (a,c): As adsorption is spontaneous, ΔG for the process is –ve. Adsorption is accompanied by decrease in randomness, therefore ΔS and $T\Delta S$ for the process is also negative. As ΔS for the process is –ve and the process is spontaneous, ΔH for the process has to be –ve (and $\Delta H > T\Delta S$ in magnitude) *i.e.*, enthalpy of the system decreases.

26. (b) : In the graph of $\Delta_f G^\circ$ *vs* T for formation of oxides, the Cu_2O line is almost at the top. So, it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke as the lines of C, CO and C, CO_2 lie below Cu, Cu_2O at much lower temperature (500-600 K).

$Cu_2O + C \longrightarrow 2Cu + CO$

27. (b) : Silver ore is oxidised by using oxygen from air as follows :

$4Ag + 8NaCN + 2H_2O + O_2(air) \longrightarrow \underset{\text{Sodium argentocyanide}}{4Na[Ag(CN)_2]} + 4NaOH$

$Ag(0) \xrightarrow{oxidation} Ag(+1)$

Silver is precipitated from the solution by addition of Zn powder in a finely divided condition.

$2Na[Ag(CN_2)] + Zn \longrightarrow \underset{\text{Sodium zinc cyanide}}{Na_2[Zn(CN_4)]} + 2Ag$

$Ag(+1) \xrightarrow{reduction} Ag(0)$

28. (d) : The impure metal is made anode while a thin sheet of pure metal acts as cathode. On passing the current, the pure metal is deposited on the cathode and equivalent amount of the metal gets dissolved from the anode.

29. (a) : $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow{Cl_2}$

$CH_2Cl-\overset{*}{\underset{\underset{CH_3}{|}}{CH}}-CH_2CH_3 +$

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{*}{\underset{\underset{Cl}{|}}{CH}}-CH_3$

30. (b) : S_N2 order for reactions are 3° < 2° < 1° methyl halide follows S_N2 mechanism. In S_N2 reactions inversion in configuration occurs.

31. (a) : In S_N2 reactions, the nucleophile attacks from back side resulting in the inversion of molecule. Also, as we move from 1° alkyl halide to 3° alkyl halide, the crowding increases and $+I$ effect increases which makes the carbon bearing halogen less positively polarised and hence less readily attacked by the nucleophile.

32. (d) : Smaller the value of pK_b, stronger is the base. Aliphatic amines are stronger bases

than ammonia due to +*I* effect of alkyl groups leading to high electron density on the nitrogen atom. Aromatic amines are weaker bases than ammonia as the lone pair of electrons on the nitrogen atom gets delocalized over the benzene ring and thus is less easily available for protonation.

33. (b) : Charge required to reduce

$Al^{3+} + 3e^- \longrightarrow Al$

1 mole of Al^{3+} to Al ; $Q = 3 \times F = 3 \times 96500$

$= 289500$ C

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

1 mole of MnO_4^- to Mn^{2+}; $Q = 5 \times F$

$= 5 \times 96500 = 482500$ C

$$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

1 mole of H_2O to O_2; $Q = 2 \times F$

$= 2 \times 96500 = 193000$ C

$$FeO + \frac{1}{2}H_2O \longrightarrow \frac{1}{2}Fe_2O_3 + H^+ + e^-$$

1 mole of FeO to Fe_2O_3

$Q = 1 \times F = 96500$ C

34. (c) :

Molecule	Total no. of e^-s pairs around *X*	Bond pairs	Lone pairs	Shape
XY	4	1	3	Linear
XY_3	5	3	2	Bent T-shaped
XY_5	6	5	1	Square pyramidal
XY_7	7	7	0	Pentagonal bipyramidal

35. (b) : $[Co(en)_2Cl_2]^+$ exists in *cis*-and *trans*-isomers out of which only *cis*-isomer will show optical activity.

36. (d) : SO_2 is a reducing agent while SO_3 is an oxidising agent. Only SO_2 bleaches the articles by reduction.

37. (a) : As physisorption involves only van der Waals forces of attraction and no chemical change, the process is exothermic but the enthalpy of adsorption is quite low (20-40 kJ mol^{-1}) as compared to (200-400 kJ mol^{-1}) in case of chemisorption.

38. (c) : Thermosetting plastics are cross-linked high polymers formed from their monomers by condensation polymerization. In these polymers the chains are held together by strong covalent bonds. Bakelite is also a condensation polymer and formed by condensation polymerization of formaldehyde and phenol.

39. (b)

40. (d) : In strongly acidic solutions, aniline becomes less reactive towards electrophilic reagents.

The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

41. (2) : No. of B^- ions in unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Now A^+ ion occupies 25% of tetrahedral holes

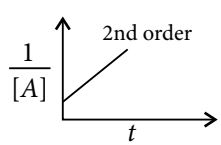
$$= \frac{8 \times 25}{100} = 2$$

Thus, ratio of B^- to A^+ is 2 : 1 or formula is AB_2.

42. (4) : 2-Methylpentanal, cyclohexanone, 1-phenylpropanone and phenylacetaldehyde contain α-hydrogen atoms and hence undergo aldol condensation.

43. (6) : EDTA is a hexadentate ligand.

44. (2) :



45. (3) : $6KOH + 3Cl_2 \xrightarrow[\text{(hot and conc.)}]{} 5KCl + KClO_3 + 3H_2O$

46. (3) : Three compounds are optically active.

$CH_3CH_2\overset{*}{C}H(CH_3)N(CH_3)C_2H_5$

$[Ph(CH_3)(C_2H_5)\overset{+}{N}H]I^-$

$C_6H_5(CH_3)(C_2H_5)\overset{+}{N}-O^-$

47. (2) : Given : Weight of solute (W_B) = 0.15 g; Weight of solvent (W_A) = 15 g; Change in the boiling temperature (ΔT_b) = 0.216 °C ; Molal elevation constant (K_b) = 2.16 °C

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

$$= \frac{2.16 \times 0.15 \times 1000}{0.216 \times 15} = 100 \text{ g or } 1 \times 10^2 \text{ g}$$

48. (8) : $CH_3-CH_2-CH_2-CH_2-CH_2-Cl$

$CH_3-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$

$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-Cl$

$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-Cl$

49. (3) : $Hg_2(NO_3)_2 \rightleftharpoons Hg_2^{2+} + 2NO_3^-$

Total ions = 3

50. (1) : $H_2 + 2Ag^+ \longrightarrow 2H^+ + 2Ag$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF}\log\frac{1}{[Ag^+]^2}$$

$$0.62 = 0.80 + 0.06 \log [Ag^+]$$

$$\text{or} \quad \log[Ag^+] = \frac{-0.18}{0.06} = -3$$

$$\text{or} \quad [Ag^+] = 1.0 \times 10^{-3}\ \text{M}$$

$$= 1.0 \times 10^{-3} \times 108 = 0.108\ \text{g L}^{-1}$$

$\therefore$ Amount of Ag in 100 mL solution = 0.0108 g

$$\therefore \ \%\ \text{Ag} = \frac{0.0108}{1.08} \times 100 = 1\%$$

SOLUTIONS TO DECEMBER 2014 CROSSWORD

	M									P								
	E					H	Y	D	R	O	G	E	N					
	T									S			E			C		F
	H	Y	D	R	O	C	H	L	O	R	I	C		O			H		E
	A		I				Y				T			N			L		R
	N		P				D				R						O		R
S	E	C	O	N	D	A	R	Y			O						R		U
			L				O				N			B	A	R	I	U	M
			E				G			G							N		
						B	E	N	Z	A	L	D	E	H	Y	D	E		
	B				N		N			L									
	R				I		B			L						L			G
	E	L	E	C	T	R	O	P	H	I	L	I	C			E			I
	A		L		R		N			U			O			A			L
	T		I		I		D			M		V	A	N	A	D	I	U	M
	H		M		C		I						G						A
	A	M	I	N	O		N						U						N
	L		N		X		G				S	U	L	P	H	U	R		
	Y		A		I								A						
	S		T		D								T						
	E		I		E		R	E	V	E	R	S	I	B	L	E			
	R		O										O						
			N					S	U	S	P	E	N	S	I	O	N		

Winners of December 2014 Crossword

Arkaprava Mahapatra, Bankura (West Bengal)

Kashish Arora, Ambala Cantt. (Haryana)

Suraj Chatterjee, Kolkata (West Bengal)

Senders of December 2014 Crossword

Muhammad Haneefa. A. (Kerala)

Devjit Acharjee, Kolkata (West Bengal): The idea is very innovative. It is like 'oxygen' to all chemistry lovers. By solving it, anyone can enhance his knowledge in chemistry.

Divya Acharya, Palampur (Himachal Pradesh): It was a wonderful experience for me. I enjoyed it a lot.

ADVANCED CHEMISTRY BLOC

(GASEOUS STATE)

Mukul C. Ray, Odisha

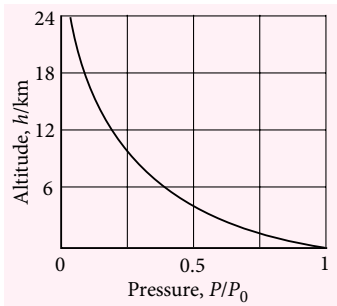
Performance of Atmospheric Air - Know Your Air

This is a concept of our day-to-day life. The barometric formula is

$$P = P_0 e^{-h/H}$$

where P_0 is the pressure at the sea level and $H = \frac{RT}{Mg}$ which is about 8 km. Here, T is the temperature, g is the acceleration due to gravity and M is the average molar mass of air, which is around 29 grams per mole.

It implies that the pressure and the density fall to about half at a height of about 6 km.



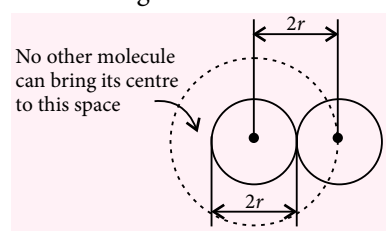
Variation of pressure with altitude as predicted by barometric formula

Now one important point is, moist air is less dense than dry air. At a given temperature and pressure, a given volume of air contains same number of molecules as per Avogadro's hypothesis. But most of the molecules of air have higher molar mass than water. By water coming in, the average molar mass of air decreases.

The term "weather", means local variation of pressure, temperature and composition of air. A small region of air is termed as "parcel". When a parcel of warm air rises, it expands and uses its own energy to push back the molecules of surroundings and gets cooled. Cool air can absorb lower concentration of water vapour than warm air. Thus water vapours accumulate to form cloud. That is why a cloudy sky is seen as rising air and clear sky as descending air.

van der Waals Constants

The van der Waals equation is a semi-empirical equation because the ideal gas laws on which it is based can be derived from pure theory, but '*a*' and '*b*' are empirical parameters found by trial and error method. One can start with any plausible estimates for '*a*' and '*b*', vary them, compare the results with the measured P, V and T behaviour, and select the values that give the best agreement with the experimental findings.



The space shown above with radius 2*r* is wasted for two molecules

About van der Waal constant '*b*' the logic is, in case of ideal gas, the entire volume of the container is available for molecules to move about as the molecules occupy negligible volume. But in real gas, molecular volume cannot be neglected. The subtracted volume for a single molecule is four times the molecular volume. For one mole of molecules, the subtracted volume is '*b*'.

It is well known that, pressure correction is due to intermolecular attraction. For some gases, values of '*a*' and '*b*' vary as :

Value of '*a*' (in atm L^2 mol^{-2})

$SO_2 > Cl_2 > C_2H_6 > NH_3 > CO_2 > CH_4 > O_2 > N_2 > H_2 > He$

Value of '*b*' (in L mol^{-1})

$C_2H_6 > SO_2 > Cl_2 > CH_4 > CO_2 > N_2 > NH_3 > O_2 > H_2 > He$

The order might be different in different books but this one is absolutely correct.

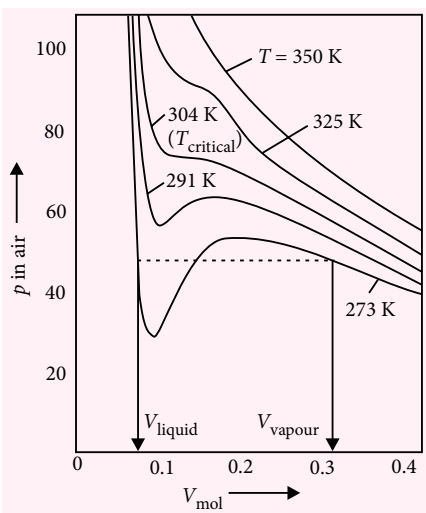
Note : Both '*a*' and '*b*' decrease with increase in temperature but '*a*' decreases much more rapidly than '*b*'.

Critical Temperature of Gas and its Implication

With slight mathematical manipulation van der Waals equation can be converted to a cubic equation of volume.

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

For any given P at constant temperature, three values of V will be there, either all are real or one real, two imaginary (imaginary values always appear in pairs). Now when plotted, the graph looks like the one shown below.



Isotherms of carbon dioxide according to the van der Waals equation

As temperature increases, these values of V come closer and at one stage they coalesce to a single point. The temperature at which this happens is called the **critical temperature** of gas.

For CO_2 this temperature is 304 K. But the oscillations, the van der Waal loops, are unrealistic. For example; an increase in pressure cannot lead to an increase in volume (P-V diagram cannot have a positive slope).

Significance :

- At the critical temperature, the gaseous state appears to transform continuously into condensed state and there is no visible surface between the two states of matter.
- The densities of the gas and the liquid states of the same matter are identical at this temperature.
- A gas cannot be condensed to liquid by application of pressure unless the temperature is less than the critical temperature.
- Easily liquefiable gases have higher critical temperature. For example, in case of ammonia it is 132 °C and for hydrogen it is –240 °C.
- Most practical significance is, it is used to distinguish between vapour and gas as :
  - A vapour is the gaseous phase of a substance below its critical temperature.
  - A gas is the gaseous phase of a substance above its critical temperature.
  - The pressure and the molar volume at the critical temperature are called **critical pressure** and **critical volume** respectively for the substance.

  Note : Critical temperature of water is 373 °C and the vapour pressure at this temperature is 218 atm.

Collision Frequency and Mean Free Path

Considering 'z' is the average number of collisions one molecule make in a unit time in unit volume and 'λ' as the mean free path that is the average distance travelled between two collisions, it can be written that

$$V_{av} = \frac{\text{Distance between collisions}}{\text{Time between collisions}}$$

$$= \frac{\text{Mean free path}}{\text{Time of flight}} = \frac{\lambda}{1/z}$$

By applying kinetic model,

$$\lambda = \frac{kT}{\sigma P}$$

where σ is the collision cross-section (it is equal to πd^2,where d is the distance between the centres of the two colliding molecules) and k is the Boltzmann constant. Thus

$$z = \frac{\sigma V_{av} P}{kT}$$

Note : Some books write it as $\frac{\sqrt{2}\sigma V_{av} P}{kT}$. The equation looks totally different. The logic is very simple. When two molecules are moving towards each other in a straight axis with velocity V_{av}, the relative velocity of one is $2V_{av}$. This means when the collisions are head on the velocity becomes $2V_{av}$. For other orientations it would have lower values. It turns out that in an average collision, the molecules move at right angle to each other and the relative speed is $\sqrt{2}V_{av}$. So surely this a better equation. But to learn the effect of temperature and pressure it is considered as given.

The consequences of these equations are summarised below :

- As $\lambda \propto 1/P$, the mean free path decreases as the pressure increases.
- As $z \propto P$, the collision frequency increases with the pressure of the gas.
- As $z \propto V_{av}$ and $V_{av} \propto \frac{1}{\sqrt{M}}$

  Heavy molecules have lower collision frequency than light molecules.

Now there is a slight variation :

If z is the number of collisions (not the number of collisions a single molecule is making) taking place per unit volume per unit time (sometimes this z is also called as collision frequency but strictly writing the former should be written as z_1 and the latter as z_{11})

$$z_{11} = \frac{\sigma V_{av} P^2}{2k^2T^2}$$

The term P/kT is the number density. For one molecule, the number of collisions is given by the expression of z above. Following unitary method, for all molecules, it should be multiplied by P/kT. But by the way each collision is counted twice hence there comes a denominator 2. From this equation again it can be concluded that

- At constant temperature, $z_{11} \propto P^2$
- For constant pressure, $z_{11} \propto T^{-3/2}$
- For variable pressure, $z_{11} \propto T^{1/2}$

Note : Those books, which write z as $\frac{\sqrt{2}\sigma V_{av} P}{kT}$, would now write z_{11} as $\frac{\sigma V_{av} P^2}{\sqrt{2}k^2T^2}$

Viscosity of Gas Increases with Temperature

For liquids, the viscosity decreases with increase in temperature, whereas for gases it increases with increase in temperature. The viscous resistance in fluids is due to the intermolecular cohesion and the molecular momentum transfer in the direction normal to the flow. Since in liquids the molecules are closely packed, the molecular effects are less and the viscous effect is mainly due to intermolecular attraction. When temperature increases cohesion decreases and hence for liquids viscosity decreases with increase in temperature.

In gases the molecules are widely spread and hence molecular cohesion forces are negligible. Since the molecular activity increases with increase in temperature, viscosity of gas increases with increase in temperature in the low-pressure range.

PRACTICE PROBLEMS 2015

Chemistry Olympiad

1. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum e.m.f.?

(a) 0.1 M HCl (b) 0.1 M CH_3COOH

(c) 0.1 M H_3PO_4 (d) 0.1 M H_2SO_4

2. Consider oxidation of following compounds :

I. $CH_2{=}CHCH_2OH \xrightarrow{A} CH_2{=}CHCHO$

II. $(CH_3)_3COH \xrightarrow{B} CH_3C(CH_3){=}CH_2$

III. $CH_3CH_2OH \xrightarrow{C} CH_3COOH$

IV. $CH_3CH{=}CHCH_3 \xrightarrow{D} CH_3COOH$

A, *B*, *C* and *D* are oxidising agents which are respectively

	A	*B*	*C*	*D*
(a)	MnO_2	Cu/Δ	H_2CrO_4	$KMnO_4$/Δ
(b)	Cu/Δ	MnO_2	H_2CrO_4	$KMnO_4$/Δ
(c)	MnO_2	Cu/Δ	$KMnO_4$/Δ	H_2CrO_4
(d)	MnO_2	H_2CrO_4	Cu/Δ	$KMnO_4$/Δ

3. Which is not correctly matched?

(1) Basic strength of oxides : $Cs_2O < Rb_2O < K_2O < Na_2O < Li_2O$

(2) Stability of peroxides : $Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2$

(3) Stability of bicarbonates : $LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$

(4) Melting point : NaF < NaCl < NaBr < NaI

(a) 1 and 4 (b) 1 and 3

(c) 1 and 2 (d) 2 and 3

4. For the reaction $2A \longrightarrow B + 3C$; if $-\frac{d[A]}{dt} = k_1[A]^2$; $\frac{d[B]}{dt} = k_2[A]^2$; $\frac{d[C]}{dt} = k_3[A]^2$ the correct relation between k_1, k_2, and k_3 is

(a) $k_1 = k_2 = k_3$ (b) $2k_1 = k_2 = 3k_3$

(c) $4k_1 = k_2 = 3k_3$ (d) $\frac{k_1}{2} = k_2 = \frac{k_3}{3}$

5. A yellow solid known to be a single compound is completely insoluble in hot water but dissolves in hot dilute HCl to give an orange solution. When this solution is cooled, a white crystalline ppt. is formed. This white ppt. redissolves on heating the solution. The compound is

(a) $Fe(OH)_3$ (b) $PbCrO_4$

(c) K_2CrO_4 (d) $Co(OH)_2$

6. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives

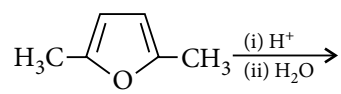
(a) $Al^{3+} + Cl^-$

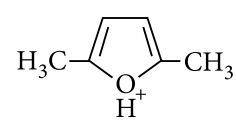
(b) $[Al(H_2O)_6]^{3+} + Cl^-$

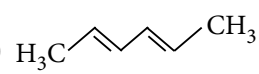
(c) $[Al(OH)_6]^{3-} + HCl$

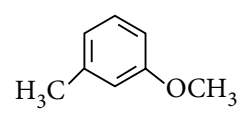
(d) $Al_2O_3 + HCl$

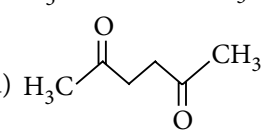
7. The major product of the following reaction is



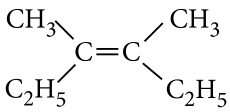
(a) 

(b) 

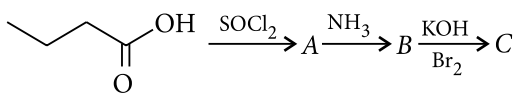
(c) 

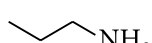
(d) 

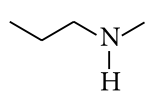
8. If a complex formed by one Ni^{2+} ion and some Cl^- ions and some PPh_3 molecules does not show geometrical isomerism and its solution does not show electrical conductance then, which is correct about the complex?
(a) It is square planar.
(b) It is tetrahedral.
(c) It is diamagnetic.
(d) None of the above is correct.

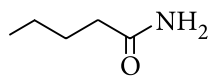
9. An alkene with molecular formula C_8H_{16} on oxidation with hot $KMnO_4$ gives acetone and 3-pentanone. The structure of the alkene is
(a) $(CH_3)_2C=C(C_2H_5)_2$
(b) 
(c) $(C_2H_5)_2C=CHCH_2CH_3$
(d) $(CH_3)_2C=CH(CH_2)_3CH_3$

10. For two gases, *A* and *B* with molecular weights M_A and M_B, it is observed that at a certain temperature, *T*, the mean velocity of *A* is equal to the root mean square velocity of *B*. Thus, the mean velocity of *A* can be made equal to the mean velocity of *B*, if
(a) *A* is at temperature *T* and *B* at *T'*, $T > T'$
(b) *A* is lowered to a temperature $T' < T$ while *B* is at *T*
(c) both *A* and *B* are raised to a higher temperature
(d) both *A* and *B* are placed at lower temperature.

11. 

In the above reaction sequence '*C*' is
(a) 

(b) 

(c) 

(d) none of these.

12. In the following reactions,
$Mg \xrightarrow[\text{Heat}]{\text{Air}} X + Y \xrightarrow{H_2O} Z$ (Colourless gas)
$Z \xrightarrow{H_2O} \text{Solution} \xrightarrow{CuSO_4} A$ (Blue coloured solution)
substances *X*, *Y*, *Z* and *A* are respectively
(a) Mg_3N_2, MgO, NH_3, $CuSO_4 \cdot 5H_2O$
(b) $Mg(NO_3)_2$, MgO, H_2, $CuSO_4 \cdot 5H_2O$
(c) MgO, Mg_3N_2, NH_3, $[Cu(NH_3)_4]SO_4$
(d) $Mg(NO_3)_2$, MgO, H_2O_2, $CuSO_4 \cdot 5H_2O$

13. Which of the following is a mixed anhydride?
(a) Cl_2O_7 (b) Cl_2O_3
(c) ClO_2 (d) Cl_2O_5

14. 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL of 0.5 N HCl solution. The excess of HCl was titrated with 0.2 N NaOH. The volume of NaOH used was 10 mL. The percentage of $Ba(OH)_2$ in the sample is
(a) 1.08 (b) 1.28
(c) 1.34 (d) 1.21

15. Decreasing order of reactivity in Williamson's ether synthesis of the following :
I. Me_3CCH_2Br II. $CH_3CH_2CH_2Br$
III. $CH_2=CHCH_2Cl$ IV. $CH_3CH_2CH_2Cl$
(a) III > II > IV > I (b) I > II > IV > III
(c) II > III > IV > I (d) I > III > II > IV

16. If 15/16 quantity of a radioactive element disintegrates in two hours, its half life would be
(a) 1 hour (b) 45 min
(c) 30 min (d) 15 min.

17. Which among the following is a hydride?
(a) Rogalite (b) Nitrolim
(c) Hydrolith (d) Minium

18. Inorganic graphite is
(a) $B_3N_3H_6$ (b) B_2H_6
(c) BN (d) BF_3

19. The standard molar enthalpies of formation of cyclohexane$_{(l)}$ and benzene$_{(l)}$ at 25°C are –156 and 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene$_{(l)}$ at 25°C is –119 kJ mol^{-1}. The magnitude of resonance energy of benzene is
(a) –152 kJ (b) 152 kJ
(c) 201 kJ (d) –201 kJ

20. Hyperconjugation is most useful for stabilizing which of the following carbocations?
(a) Neopentyl (b) *tert*-Butyl
(c) Isopropyl (d) Ethyl

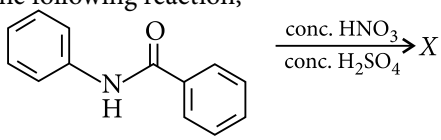
21. When the following five anions are arranged in order of decreasing ionic radius, the correct sequence is

(a) Se^{2-}, I^-, Br^-, O^{2-}, F^-
(b) I^-, Se^{2-}, O^{2-}, Br^-, F^-
(c) Se^{2-}, I^-, Br^-, F^-, O^{2-}
(d) I^-, Se^{2-}, Br^-, O^{2-}, F^-

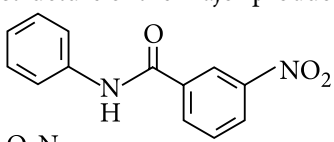
22. The distance between an octahedral and tetrahedral voids in *fcc* lattice would be

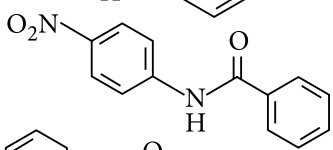
(a) $\sqrt{3}\,a$ (b) $\frac{\sqrt{3}a}{2}$ (c) $\frac{\sqrt{3}a}{3}$ (d) $\frac{\sqrt{3}a}{4}$

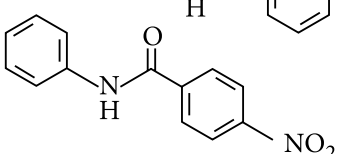
23. In the following reaction,

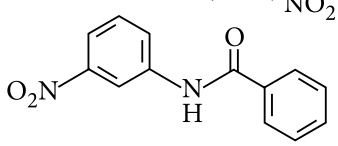


the structure of the major product *X* is

(a)


(b)


(c)


(d)


24. There is loss in weight when mixture of Li_2CO_3 and $Na_2CO_3.10H_2O$ is heated strongly. This loss is due to

(a) Li_2CO_3 (b) $Na_2CO_3.10H_2O$
(c) both (a) and (b) (d) none of these.

25. While testing BO_3^{3-}, there is green-edged flame on heating the salt with conc. H_2SO_4 and C_2H_5OH. Green colour is of

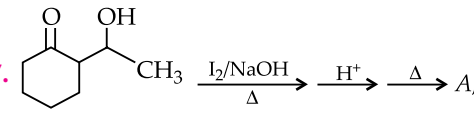
(a) $(CH_3)_3B$ (b) $(C_2H_5O)_3B$
(c) B_2O_3 (d) H_3BO_3

26. Of the following reduction processes,

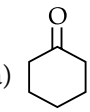
(I) $Fe_2O_3 + C \rightarrow Fe$ (II) $ZnO + C \rightarrow Zn$
(III) $Ca_3(PO_4)_2 + C \rightarrow P$
(IV) $PbO + C \rightarrow Pb$

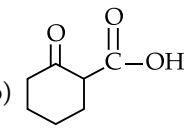
Correct processes are

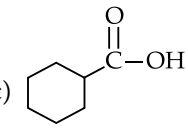
(a) (I), (II), (IV) (b) (I), (II), (III)
(c) (II), (IV) (d) all of these.

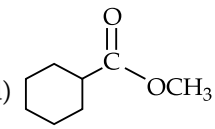
27.


A is

(a)


(b)


(c)


(d)


28. A 300 mL solution of NaCl was electrolysed for 6 minutes. If the pH of the final solution was 12.24, the average current used is

(a) 5 A (b) 1.32 A
(c) 1.4 A (d) 1.29 A

29. Chlorination of propane is carried out in the presence of sunlight. The % yield of major and minor alkyl halides will be

(a) 92 %, 8 % (b) 70 %, 30 %
(c) 80 %, 20 % (d) 86 %, 14 %

30. pK_a values of CH_3COOH, CCl_3COOH, C_6H_5OH and $C_6H_5SO_3H$ are 4.79, 0.9, 10.0 and –2.6. The leaving tendency of their conjugate bases increases in the order

(a) $C_6H_5O^- < CH_3COO^- < CCl_3COO^- < C_6H_5SO_3^-$
(b) $C_6H_5O^- < C_6H_5SO_3^- < CH_3COO^- < CCl_3COO^-$
(c) $CCl_3COO^- < C_6H_5O^- < C_6H_5SO_3^- < CH_3COO^-$
(d) $CCl_3COO^- < CH_3COO^- < C_6H_5SO_3^- < C_6H_5O^-$

ANSWER KEY

1. (d)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (b)
6. (b)	**7.** (d)	**8.** (b)	**9.** (a)	**10.** (b)
11. (a)	**12.** (c)	**13.** (c)	**14.** (b)	**15.** (c)
16. (c)	**17.** (c)	**18.** (c)	**19.** (a)	**20.** (b)
21. (d)	**22.** (d)	**23.** (b)	**24.** (c)	**25.** (b)
26. (d)	**27.** (a)	**28.** (c)	**29.** (a)	**30.** (a)

CHEMISTRY MUSING

SOLUTION SET 17

1. (d) **2.** (c)

3. (c) : According to Raoult's law;

$$\frac{p^\circ - p}{p^\circ} = x_2 \Rightarrow \frac{74.66 - 74.01}{74.66} = x_2$$

If M is the molar mass of hydrocarbon, then

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{2/M}{(100/78) + (2/M)}$$

$$\therefore \quad \frac{74.66 - 74.01}{74.66} = \frac{2/M}{(100/78) + (2/M)}$$

$$\Rightarrow \quad M = 177.7 \text{ g mol}^{-1}$$

$$m_C : m_H = 94.4 : 5.6$$

Thus, atomic ratio is $N_C : N_H = \frac{94.4}{12} : \frac{5.6}{1}$

$$= 7.87 : 5.6 = 1.4 : 1 = 7 : 5$$

Hence, empirical formula is C_7H_5.

Empirical formula mass = 89 g mol^{-1}

$$\text{No. of } C_7H_5 \text{ units} = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

$$= \frac{177.7}{89} \approx 2$$

Hence, molecular formula = $C_{14}H_{10}$

4. (b) : $(CH_3)_3CBr + NaOC_2H_5$ cannot be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.

$$(CH_3)_3CBr \xrightarrow{^-OC_2H_5} (CH_3)_2C{=}CH_2 + HBr$$

In the reaction of *iso*-butene with ethanol, *iso*-butene will form *tert*-butyl cation which reacts with ethanol, a nucleophile to form ether.

$$(CH_3)_2C{=}CH_2 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_3$$

$$\xrightarrow[\text{(ii) } -H^+]{\text{(i) } CH_3CH_2OH} (CH_3)_3COCH_2CH_3$$

5. (c)

6. (b) : Volume of the room = $10 \times 15 \times 4 = 600$ m^3

$$= 60 \times 10^4 \text{ L}$$

Moles of air in the room at 25°C and 1 atm pressure,

$$n = \frac{PV}{RT} = \frac{1 \times 60 \times 10^4}{0.0821 \times 298} = 2.45 \times 10^4$$

Heat produced in one second by each student = 200 joules

Heat produced in one second by 60 students = $200 \times 60 = 12000$ joules

Heat produced in 20 minutes = $12000 \times 20 \times 60$

$$= 144 \times 10^5 \text{ joules}$$

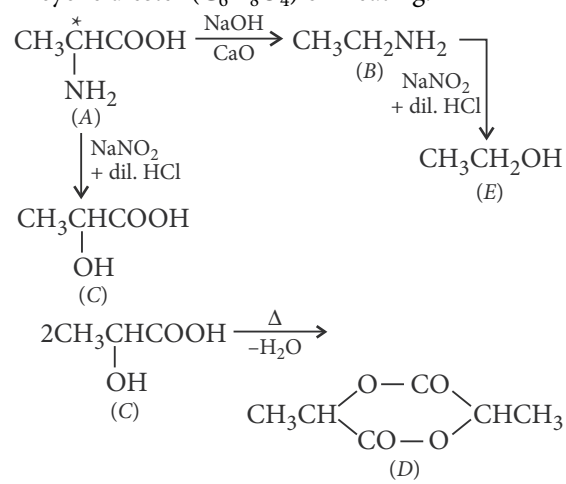
$\therefore$ Change in enthalpy of air, $\Delta H = n \cdot C_p \cdot \Delta T$

$$144 \times 10^5 = 2.45 \times 10^4 \times \frac{7}{2} \times 8.314 \times \Delta T$$

$\therefore \quad \Delta T = 20.2$ K

7. (c) **8.** (a)

9. (2) : Since (*A*) forms hydrochloride and dissolves in water to give a neutral solution, it contains both a basic and an acidic functional groups. It is likely to be an amino acid as the molecular formula contains one N and two O-atoms. On decarboxylation it forms an amine (*B*). Therefore, (*B*) is a saturated amine. (*B*) reacts with $NaNO_2$ and dilute HCl forming (*E*), C_2H_5OH. Thus, (*B*) is $CH_3CH_2NH_2$. (*A*) also reacts with $NaNO_2$ and dilute HCl forming (*C*), a hydroxy acid which forms a cyclic diester ($C_6H_8O_4$) on heating.



Thus in (*A*), the N of $-NH_2$ group is attached to a 2° C-atom.

10. (5) : $Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$

$$K_f = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4} = 2 \times 10^9$$

$$\frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]} = [NH_3]^4 \times 2 \times 10^9$$

$$= 10^4 \times 2 \times 10^9 = 2 \times 10^{13}$$

$$\frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = 5 \times 10^{-14}$$

At a Glance CHEMISTRY today 2014

MONTHS	Solved Papers (2014)	Practice Papers (2014 & 2015)	Examiner's Mind	JEE Foundation Series	Concept Map	Others
JANUARY	—	AIPMT, CBSE Board Chapterwise Series -8 (2014)	Hydrocarbons, Environmental Chemistry (Class XI); Amines, Biomolecules, Polymers, Chemistry in Everyday Life (Class XII)	Unit-7 : Organic Compounds Containing Oxygen, Organic Compounds Containing Nitrogen	Equilibrium	NCERT Xtract, Chemistry Musing Problem Set-6, You Asked, We Answered, Competition Corner, Concept Booster, Chemistry Musing Solution Set-5
FEBRUARY	—	JEE Main, CBSE Board Series-9 (2014)	—	Unit-8 : Biomolecules, Polymers, Chemistry in Everyday Life	General principles and processes of isolation of elements	NCERT Xtract, You Asked, We Answered, Learn Fast (Chemical Kinetics), NCERT Corner (Class XI-XII), Concept Booster, Competition Corner, Chemistry Musting Problem Set-7, Chemistry Musing Solution Set-6, Essential Reactions for Competitive Exams
MARCH	—	JEE Main, JEE Advanced, AIPMT, CBSE Board-Sample Paper (2014),	—	Principles Related to Practical Chemistry	The Solid State	Chemistry Musing Problem Set-8, Competition Corner, You Asked, We Answered, NCERT Corner (Class XI-XII), Chemistry Musing Solution Set-7, AIIMS Special (Assertion & Reason), Concept Booster
APRIL	CBSE Board	JEE Advanced, AIIMS, AIPMT, BITSAT	—	—	Alcohols, Phenols and Ethers	Chemistry Musing Problem Set-9, JEE Final Touch Class XI (Last 3 years chapterwise questions), NCERT Corner (Class XI-XII), You Asked, We Answered, Learn Fast (Coordination Compounds), Competition Corner, Chemistry Musing Solution Set-8, Concept Booster
MAY	JEE Main	JEE Advanced, AIIMS, BITSAT (Full Length)	—	—	Aldehydes, Ketones and Carboxylic Acids	Chemistry Musing Problem Set-10, JEE Final Touch Class-XII (Last 3 years chapterwise questions), NCERT Corner (Class XI-XII), You Asked, We Answered, Periodic Table and General Trends of the Elements, Chemistry Musing Solution Set-9
JUNE	AIPMT, Kerala PET, WB-JEE	CBSE Board Chapterwise Series-1 (2015)	Some Basic Concepts of Chemistry, Structure of Atom (Class XI); The Solid State, Solutions (Class XII)	—	Organic Compounds Containing Nitrogen	Chemistry Musing Problem Set-11, You Asked, We Answered, NCERT Corner (Class XI-XII), Concept Booster, Advanced Chemistry Bloc (Polymorphism and Crystal Defects), Chemistry Musing Solution Set-10
JULY	JEE Advanced, Kerala PMT	CBSE Board Chapterwise Series-2 (2015)	Classification of Elements and Periodicity in Properties, Chemical Bonding and Molecular Structure (Class XI); Electrochemistry, Chemical Kinetics (Class XII)	Unit-1 :Some Basic Concepts in Chemistry, States of Matter, Atomic Structure, Chemical Bonding and Molecular Structure	*s*-Block Elements	AIPMT 2014 - Topper Interview, Chemistry Musing Problem Set-12, You Asked, We Answered, Chemistry Musing Solution Set-11
AUGUST	Karnataka CET	CBSE Board Chapterwise Series-3 (2015)	States of Matter, Thermodynamics (Class XI); Surface Chemistry, The *p*-Block Elements (Group 15 to 18), The *d*- and *f*-Block elements (Class XII)	Unit-2 : Chemical Thermodynamics, Solutions, Equilibrium	The *p*-Block Elements (Group 13 & 14)	Chemistry Musing Problem Set-13, Concept Booster, Chemistry Olympiad Problems, Advanced Chemistry Bloc, You Asked, We Answered, Chemistry Musing Solution Set-12
SEPTEMBER	J & K CET, AMU Engg.	CBSE Board Chapterwise Series-4 (2015)	Equilibrium, Redox Reactions (Class XI); General Principles and Processes of Isolation of Elements, Coordination Compounds, Haloalkanes and Haloarenes (Class XII)	Unit-3 : Redox Reactions and Electrochemistry, Chemical Kinetics, Surface Chemistry	General Organic Chemistry (Part-1)	Chemistry Musing Problem Set-14, Concept Booster, Chemistry Olympiad Problems, Crossword, Advanced Chemistry Bloc, You Asked, We Answered, Chemistry Musing Solution Set - 13
OCTOBER	—	CBSE Board Chapterwise Series-5 (2015)	Hydrogen, The *s*-Block Elements (Class XI); Alcohols, Phenols and Ethers, Aldehydes, Ketones and Carboxylic Acids (Class XII)	Unit-4 : Classification of Elements and Periodicity in Properties, General Principles and Processes of Isolation of Metals, Hydrogen, *s*-Block Elements, *p*-Block Elements (Group 13 and 14)	General Organic Chemistry (Part-2)	Chemistry Musing Problem Set-15, Concept Booster, Learn Fast (Thermodynamics), Chemistry Olympiad Problems, You Asked, We Answered, Advanced Chemistry Bloc, Crossword, Chemistry Musing Solution Set-14
NOVEMBER	—	CBSE Board Chapterwise Series-6 (2015)	The *p*-Block Elements (Group 13 and 14), Organic Chemistry, Some Basic Principles and Techniques (Class XI); Amines, Biomolecules (Class XII)	Unit-5 : *p*-Block Elements (Group 15 to 18), *d*-and *f*-Block Elements, Coordination Compounds, Environmental Chemistry	Hydrocarbons	Chemistry Musing Problem Set-16, Concept Booster, Advanced Chemistry Bloc, Chemistry Musing Solution Set-15, Chemistry Olympiad Problems, Crossword, You Asked, We Answered, Learn Fast (Equilibrium)
DECEMBER	—	CBSE Board Chapterwise Series-7 (2015)	Hydrocarbons, Environmental Chemistry (Class XI); Polymers, Chemistry in Everyday Life (Class XII)	Unit-6 : Purification and Characterisation of Organic Compounds, Some Basic Principles of Organic Chemistry, Hydrocarbons, Organic Compounds Containing Halogens	Structure of Atom	Chemistry Musing Problem Set-17, Learn Fast (Chemical Bonding and Molecular Structrure), Advanced Chemistry Bloc, Chemistry Musing Solution Set-16, You Asked, We Answered, Chemistry Olympiad Problems, Concept Booster, Crossword

CROSSWORD

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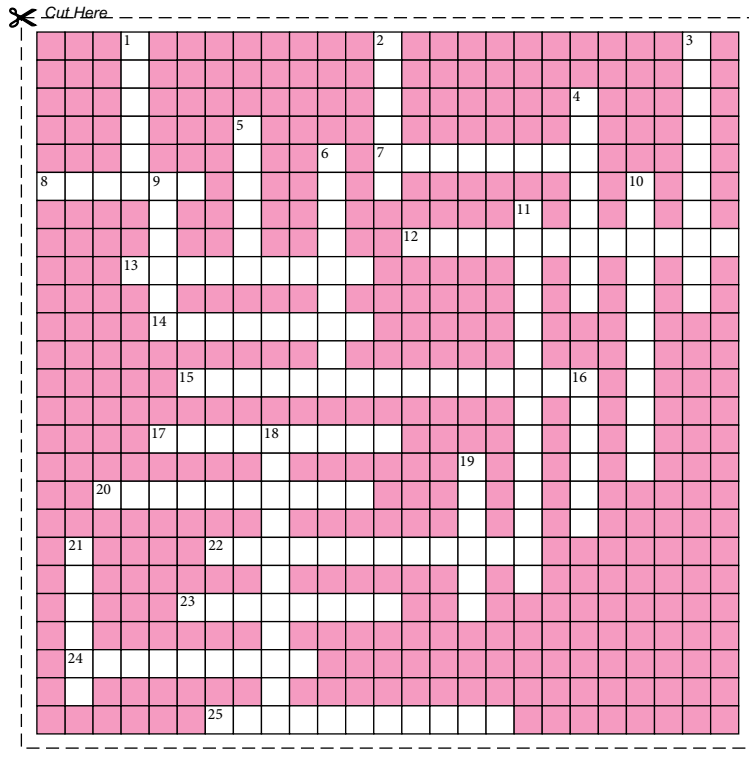

ACROSS

7. Antidote for CO poisoning. (8)

8. Crystalline SiO_2 is. (6)

12. Another name of hydrochloric acid. (12)

13. Complex nitrogenous substances, isolated from the plants which when administered into the body produce some physiological action. (9)

14. A liquid-liquid colloidal system. (8)

15. Colloidal solution of gold in water is called. (15)

17. Natural wax is also known as. (9)

20. Measures the relative densities of two liquids. (10)

22. A platonic hydrocarbon shaped like a tetrahedron and has not yet been synthesized. (12)

23. Impurity present in ruby is . (8)

24. Used in pyrotechnics, flares and photographic flashbulbs. (9)

25. Difference between the potential required for the evolution of the gas and its standard reduction potential. (11)

DOWN

1. The pressure developed inside the cell due to the inflow of water into it is called. (6)

2. An alloy used to make permanent magnets. (6)

3. Method by which lighter earthy particles are freed from the heavier ore particles by washing with water. (10)

4. Word derived from the Greek word 'kinesis' which means movement. (8)

5. A derivative of phenol present in thyme and mint. (6)

6. $Mg(ClO_4)_2$ is used as a drying agent under the name. (9)

9. The number of five membered rings in fullerene. (6)

10. Disease caused by the deficiency of essential amino acids. (11)

11. A dye formed when C_6H_5CHO reacts with dimethylaniline. (14)

16. Freon-12, the most widely used refrigerant is manufactured from carbon tetrachloride by _____ reaction. (6)

18. A leaving group such as H^+ which departs without an electron pair is called an. (11)

19. A waste product from steel industry having properties similar to cement. (6)

21. The amount of space taken up by an object. (6)

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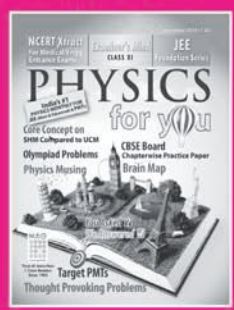

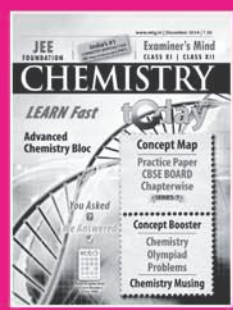

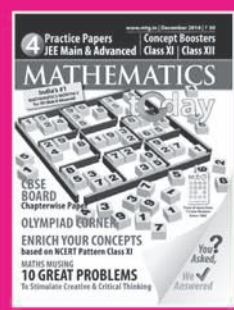

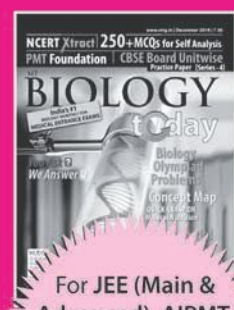

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